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FERROELEKTRİK SERAMİK İNCE FİLMLER

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PROF. DR. MACİT ÖZENBAŞ

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ANKARA

ÖNSÖZ

Bu raporda TÜBİTAK tarafından desteklenen "Ferroelektrik Seramik İnce Filmler" konusundaki çalışmaların sonuçları verilmektedir. Şubat 1994 – Şubat 1998 tarihleri arasında sürdürülen bu çalışma ferroelektrik seramik oksitlerden Pb(Zr,Ti)O_3 (PZT) sistemi üzerindeki ince film çalışmalarını yansıtmaktadır.

Çalışmaların yürütülmesi sırasında idari yönden gösterdikleri anlayışlı tutumlarından dolayı MİSAG Yürütme Komitesi Sekreteri Prof. Dr. Önder ÖZBELGE'ye, ayrıca idari yönlerdeki katkılarından ötürü Feridun GÖRGÜLÜ ve diğer MİSAG çalışanlarına teşekkür ederim.

Proje çalışmaları sırasında ODTÜ Metalurji ve Malzeme Mühendisliği Bölümündeki mevcut atölye ve laboratuvar olanakları için Bölüm Başkanlığına teşekkür ederim.

Proje yöneticisi olarak, proje çalışmalarının her evresinde yılmadan gayret gösteren proje çalışanlarına (S. Ümit ERGİN, Tufan GÜNGÖREN, Ercan TAŞPINAR ve Nilgün TURHAN) projeye yaptıkları doğrudan veya dolaylı katkıları için teşekkür ederim.

İÇİNDEKİLER

TABLO LİSTESİ

ŞEKİL LİSTESİ

Sayfa

ÖZ

Bu çalışmada ferroelektrik özellikli $Pb(Zr,Ti)O_3$ filmler ve tozlar sol-jel yöntemi kullanılarak elde edilmiştir. Tozlar sulu çözeltiden homojen çökeltme, filmler ise çökelme öncesi daldırma yöntemi kullanılarak üreli ortamda hazırlanmışlardır. Altlık malzemesi olarak platin kaplanmış Si-(111) dilimleri, Si dilimleri ve α-Al_2O_3 kullanılmıştır.

Filmlerin ve tozların karakterizasyon işlemleri için öncelikle XRD ve SEM/EDS kullanılmıştır. Parça boyutu, morfolojisi ve film yüzeyleri SEM çalışmaları ile gözlemlenmiş, film ve toz bileşimleri EDS analizleri alınarak araştırılmıştır. Isıl işlem esnasında bir kaç kez XRD analizleri alınarak oluşan fazlar belirlenmiştir. Toz örneklerin içerdiği safsızlıkların belirlenebilmesi amacı ile spektroskopik IR analizleri yapılmıştır.

850°C'de, 5 saat boyunca ısıl işleme tabi tutulmuş bütün tozlar ve filmlerin perovskit faza geçerek tamamen kristalize olduğu ve stokiyometrik olduğu belirlenmiştir. 350°-650°C ısıl işlem sıcaklıkları arasında perovskit, piroklor, ve kurşun titanyum, 650-850°C arasında ise perovskit ve piroklor fazlar gözlemlenmiştir. Hazırlanan PZT tozların küçük, düzgün ve homojen dağılımlı parça yapısında olduğu, ancak filmlerin bileşimlerinin yer yer homojen olmadığı belirlenmiştir. Platin kaplanmış silisyum ve alumina altlıklar üzerindeki ıslanmanın, platin kaplanmamış silisyum üzerindekine göre daha fazla olduğu gözlemlenmiştir.

Platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmlerin polarizasyon histeresis eğrisinden elde edilen artık polarizasyon (P_r) ve koersiv alan (E_c) değerleri, ~22 $\mu C/cm^2$ ve ~20 kV/cm, olarak belirlenmiştir. Aynı filmlerde dielektrik katsayısı ise 562 olarak hesaplanmıştır.

Anahtar Sözcükler: PZT, ferroelektrik filmler, sol-jel yöntemi.

ABSTRACT

In this study, ferroelectric $Pb(Zr,Ti)O_3$ films and powders were prepared from metal chlorides using sol-gel processing method. For powders; homogeneous precipitation from aqueous solution and for films; dip coating just before precipitation was applied in the presence of urea, $[(NH_2)_2CO]$. Pt-coated Si (111) wafers, Si wafers and α-Al_2O_3 were employed as substrates in the study.

Sol-gel processing method was used throughout the study, because it is a reliable, compositionally adjustable and inexpensive method for the production of ferroelectric films.

Characterization of the films and powders were carried out primarily by XRD and SEM/EDX. The particle size and morphology, and film surfaces were observed during SEM studies, while compositions of the films and powders were investigated by EDX analyses. Phases formed upon annealing were determined by XRD of the samples at several stages of annealing. In order to accurately determine the impurities remained in the powder samples, IR spectroscopic analyses were carried out.

Both the films and powders were stoichiometric and completely crystallized into perovskite phase after annealing for 5 hours at 850^0C. For annealing temperatures between 350 and 650^0C, perovskite, pyrochlore, lead titanate, and for those between 650 and 850°C, pyrochlore and perovskite phases were observed. The PZT powders had homogeneously distributed, fine particle sizes and morphology; however, the films prepared were partly deviated from compositional homogeneity. The films have better wetting characteristics on alumina and Pt-coated Si substrates than that on bare silicon substrates.

PZT films on platinized silicon substrates obtained by using urea showed remanent polarization and coercive field values as ~22 $\mu C/cm^2$ and ~20 kV/cm from the polarization hysteresis diagram. Dielectric constant of the same films was calculated as 562.

Keywords: PZT, Ferroelectric films, Sol-gel processing.

BÖLÜM I

GİRİŞ

Ferroelektrik seramik malzemeler genel olarak perovskit grubu yapıların karmaşık oksitlerinden oluşurlar. Hacimsel boyutlardaki ferroelektrik malzemeler üzerinde üretimleri ve özellikleri açısından çeşitli araştırmalar yapılmakta ve bazı uygulama alanlarında ticari olarak kullanılmaktadırlar. Son yıllarda bu malzemelerin mikromekanik ve mikroelektronik uygulamalar amacıyla ince film olarak hazırlanmaları da gündeme gelmiştir (O'Connor, 1993, Jenkins, et. al., 1995, Muralt, et. al., 1995). Fakat hacimsel boyutlardaki ferroelektriklerle ilgili malzeme seçimi, hazırlanması, fiziksel özelliklerinin belirlenmesi ve güvenilirlik gibi araştırmaların neticeleri ince film ferroelektriklerde doğrudan kullanılamamaktadır. Bu ince filmler çeşitli altlıklar üzerine kaplandıklarından, en azından altlık-film arayüzey reaksiyonları ortaya çıkmaktadır.

Ferroelektrik seramik ince filmler, elektrik alan uygulandığı takdirde tersine çevrilebilir spontane (kendiliğinden oluşan) bir polarizasyona sahiptir. Bu özellikleri nedeniyle kapasitör, piezoelektrik malzeme (transducer), piroelektrik dedektör, elektro-optik malzeme, termistör ve dielektrik malzeme olarak çeşitli uygulama alanlarında kullanılmaktadırlar (Scott ve Paz de Araujo, 1989, Scott, 1993). Bu nedenle projenin amacı ferroelektrik seramik ince filmlerle ilgili bir araştırmayı başlatmak ve bu filmlerin yapılarını çeşitli karakterizasyon yöntemleri ile çalışmak olarak belirlenmiştir.

1952'den 1965'e kadar olan devrede yapılan çalışmalar tek kristal ferroelektrik ya da ferroelektrik seramik malzeme üzerinde geliştirilmiş doğrudan matriks adresleme yöntemini kullanan ferroelektrik kapasitörler üzerinde yoğunlaşmıştı. Fakat elde bulunan ferroelektrik malzemelerde matriks adresleme için yeterli elektrik alan olmadığı için, bu malzemeler pratikte kullanılamadı.

1965-1975 yılları arasında yapılan çalışmalarda, bazı araştırma grupları tek kristal ya da seramik ferroelektrik malzeme üzerine yarı iletken malzemeyi kaplayarak ferroelektrik yarı iletken ince filmler üretmeye çalıştılar. 1985 yılından beri ferroelektrik ince filmlerle standart metal-oksit yarı iletken silisyum entegre devre dilimlerini birleştirmek için çalışmalar yapılmaktadır. Yapılan çalışmalar sonucunda yarı iletken dilim üzerine kaplanmış ferroelektrik ince filmin ferroelektrik malzeme üzerine kaplanan yarı iletken filmden daha pratik olduğu anlaşılmıştır. Günümüzde yapılan çalışmalar ferroelektrik malzemelerin uçucu olmaması özelliğini kullanarak ferroelektrik hafizalar üzerinde yoğunlaşmaktadır. Ferroelektrik ince filmler yüksek dielektrik katsayısına sahip oldukları için yoğunluğu fazla olan DRAM' larda kullanılmaktadırlar (Polla, 1995).

Ferroelektrik ince filmlerin kütlesel seramik malzemeye göre bazı avantajları bulunmaktadır. Her iki durumda da benzer histeresis döngüleri elde edilir; bu sebeple ferroelektrik malzemeler pek çok uygulamalarında ince film formunda yer almaktadır.

Son dönemlerde gittikçe artan oranda cihaz malzemelerin ferroelektrik özellikleri kullanılarak üretilmektedir. Ferroelektrik etki olarak tanımlanan özellik kristal malzemelere dışarıdan elektrik alan uygulandığında bu malzemelerde kendiliğinden bir polarizasyon oluşumuna neden olur ve elektrik alan kesildiğinde bu polarizasyon malzeme içinde kalır. Ters elektrik alan uygulandığında malzemedeki polarizasyon ters yöne çevrilir. Ferroelektrik malzemelerde kaydedilen bilgiler elektrik alan kesilse ve radyasyona maruz kalsa bile malzemede saklandığından, bu malzemeler hafiza uygulamaları için idealdir.

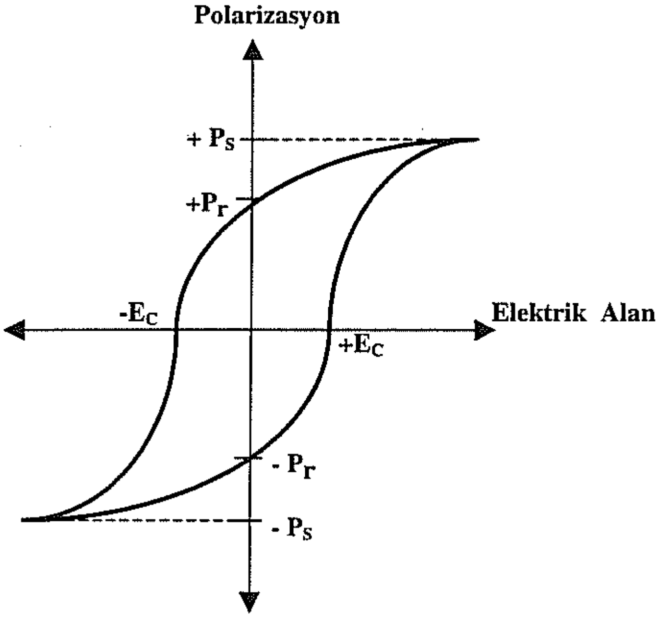
BÖLÜM II

FERROELEKTRİK MALZEMELER

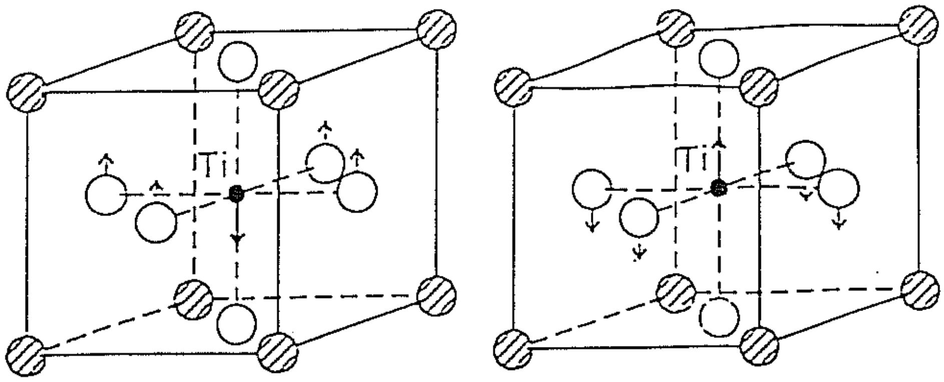
2.1. Temel Kavramlar

Ferroelektrik malzemeler, elektrik alan uygulandığı takdirde tersine çevrilebilir spontane (kendiliğinden oluşan) bir polarizasyona sahiptir. Ferroelektrik etki olarak tanımlanan bu özellik kristal malzemelere dışarıdan elektrik alan uygulandığında bu malzemelerde kendiliğinden bir polarizasyon oluşumuna neden olur ve elektrik alan kesildiğinde bu polarizasyon malzeme içinde kalır. Ters elektrik alan uygulandığında malzemedeki polarizasyon ters yöne çevrilir. Belirli bir kritik sıcaklığın (T_c) altında oluşan bu spontane polarizasyon neticesinde Şekil 2.1'de verilen histeresis döngüsü oluşur. Bu histeresis döngüsü üzerinde 3 önemli nokta göze çarpmaktadır : koersiv alan (E_c), kalıcı polarizasyon vektörü (P_r) ve saturasyon polarizasyon vektörü (P_s). Düşük elektrik alan şiddetlerinde polarizasyon değeri uygulanan alanla birlikte doğrusal olarak değişmekte ve doğrunun eğimi başlangıç dielektrik katsayısı değerini vermektedir. Elektrik alan kesildiğinde polarizasyon değeri "kalıcı polarizasyon, P_r" olarak bilinen değerde kalmaktadır. Net polarizasyon vektörünün yönünü çevirmek için gerekli olan elektrik alan değeri ise Şekil 1'de verildiği üzere koersiv alan (E_c) olarak tanımlanmaktadır (Barsoum, 1997).

Ferroelektrik davranış sürekli dipol moment hali gösteren kristal kafes yapısından kaynaklanmaktadır. Kritik sıcaklık olan T_c'nin (Curie sıcaklığı) üzerinde bu hal polar olmayan duruma dönüştüğünden bu sıcaklıklarda ferroelektrik davranış gözlenmez. T_c'nin üzerindeki sıcaklıklarda tetragonal perovskit yapı polar olmayan basit kübik yapıya dönüşmektedir. Ferroelektrik davranış gösteren tetragonal perovskit yapıda iki polarizasyon hali bulunur (Şekil 2.2). Örneğin kurşun titanat yapısında Ti^{+4} iyonları her bir kübün merkezinde, O^{-2} iyonları ise yüzey merkezlerinde yer alırlar. Ferroelektrik faz bozulmuş (distorted) tetragonal yapıdan kaynaklanır. Oda sıcaklığında kararlı olan bu yapıda Ti iyonu pozisyonunun diğer iyonlara göre kaymasından dolayı net bir dipol momenti oluşmaktadır. Böylece $PbTiO_3$ yapısında polarizasyonun "aşağı" veya "yukarı" olduğu "ferroelektrik sahalar" (ferroelectric domains) olarak adlandırılan bölgeler görülür. Bununla beraber yeteri kadar yüksek değerlerde olan elektrik alan uygulandığı zaman, bütün bu bölgeler aynı doğrultuda yönlendirilebilirler. Ferroelektrik malzemelerdeki polarizasyonun bu yön değiştirme özelliği (elektrik alanın değiştirilmesiyle 1 veya 0 olma özelliği) hafiza uygulamalarının temelini teşkil etmektedir (Buchanan, 1986).



Şekil 2.1. Kalıcı polarizasyon (P_r), satürasyon polarizasyonu (P_s) ve koersiv alan (E_c) değerlerini gösteren ferroelektrik histeresis döngüsü.



Şekil 2.2. Ferroelektrik ABO_3 perovskit yapısındaki polarizasyon halleri.

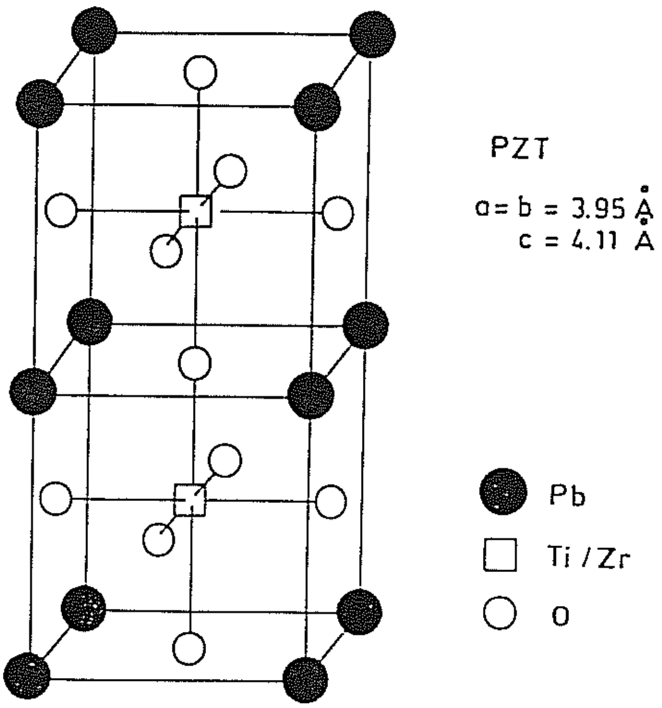
2.2. Ferroelektrik Seramiklerin Kompozisyonu

PZT, $BaTiO_3$, $PbTiO_3$, $(Sr,Ba)TiO_3$, PLT, PLZT, $Bi_4Ti_3O_{12}$ ve $Pb_5Ge_3O_{15}$ ince film olarak hazırlanan ferroelektrik seramik malzemelerin başlıcalarındandır. Düşük koersiv alan değeri veren rombohedral kompozisyonlar ile düşük dielektrik sabit ve yüksek piezoelektrik voltaj özellikleri olan tetragonal kompozisyonlar çok çeşitli biçimlerde çalışılmalarına rağmen, henüz hangi kompozisyonun hangi uygulamada kullanılabileceği konusu açıklık kazanmış değildir. En geniş şekilde araştırılan malzeme ise perovskit yapıdaki PZT katı eriyiğidir. Şekil 2.3'te yapısı verilen PZT sisteminde eşit sayıda divalent Pb^{+2} iyonları ile tetravalent Zr^{+4} ve Ti^{+4} iyonları bulunmaktadır. PZT sisteminin daha fazla araştırılmasının nedeni ise aşağıda verilmektedir :

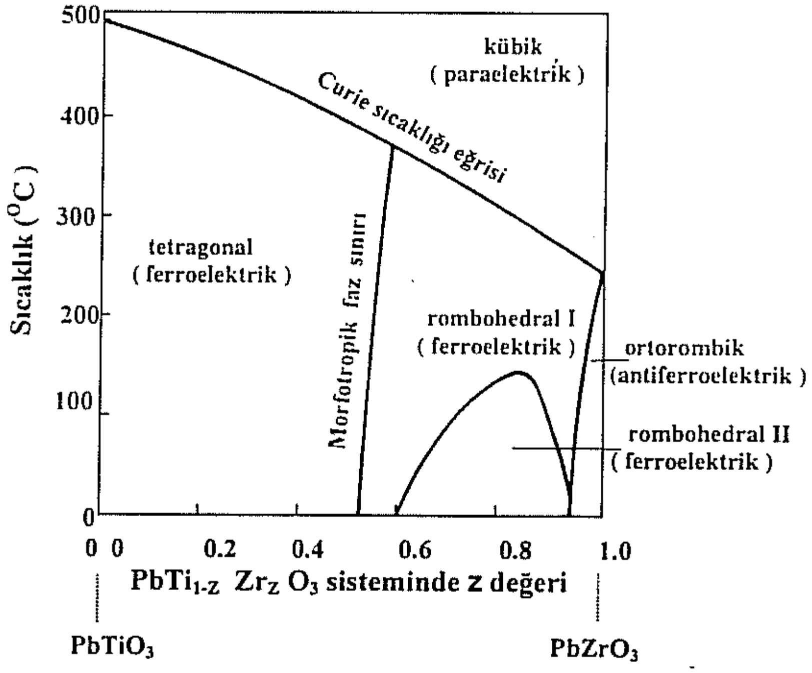
- Diğer kompozisyonlara göre daha yüksek elektromekanik kuplaj (coupling) katsayıları değerlerine sahiptir.
- Daha yüksek sıcaklıklarda çalışmayı mümkün kılan T_c (Curie sıcaklığı) değerine sahiptir.
- Kolaylıkla kutuplanabilir bir malzemedir.
- Dielektrik katsayısı değerleri geniş bir alan içerisine yayılmaktadır.
- Sinterlemesi kolay bir malzemedir.
- Çeşitli katkı elementleriyle katı eriyik oluşturabildiğinden geniş bir özellik spektrumu göstermektedir.

PZT sisteminin faz diyagramı ise Şekil 2.4'te verilmektedir. Bu faz diyagramının önemli bir özelliği MPB olarak adlandırılan morfotropik faz sınırı bölgesidir. Bu bölge sabit sıcaklıkta kompozisyona bağlı olarak yapıda meydana gelen bir değişimin görüldüğü bölgedir. Tetragonal $PbTiO_3$ ve rombohedral $PbZrO_3$ bölgeleri arasında % 52 $PbZrO_3$ mol değerinde (PZT 52/48) morfotropik faz sınırı yer almaktadır. Faz diyagramından da görülebileceği gibi PZT sistemindeki bu faz sınırı civarındaki kompozisyonların polarizasyon özellikleri Curie sıcaklığı olan yaklaşık 375°C'ye kadar kararlı kalmaktadır. Curie sıcaklığı üzerinde yapı paraelektrik özellik gösteren kübik yapıya dönüşmektedir. Bu durum ise uygulanan elektrik alan kaldırıldığında malzemenin tekrardan polarize edilmemiş haline dönüştüğü özellik olmaktadır.

PZT faz diyagramında morfotropik faz sınırından titanat ucuna doğru gidildiğinde yapı tetragonal halde, MPT sınırından zirkonat ucuna doğru gidildiğinde ise yapı rombohedral halde bulunmaktadır. Optimum piezoelektrik ve ferroelektrik özellikler morfotropik faz sınırı boyunca elde edildiğinden, bu faz sınırı etrafındaki kompozisyonlar söz konusu özellikler için en fazla araştırılan kompozisyonlar olmaktadır (Jaffe, et. al., 1971).

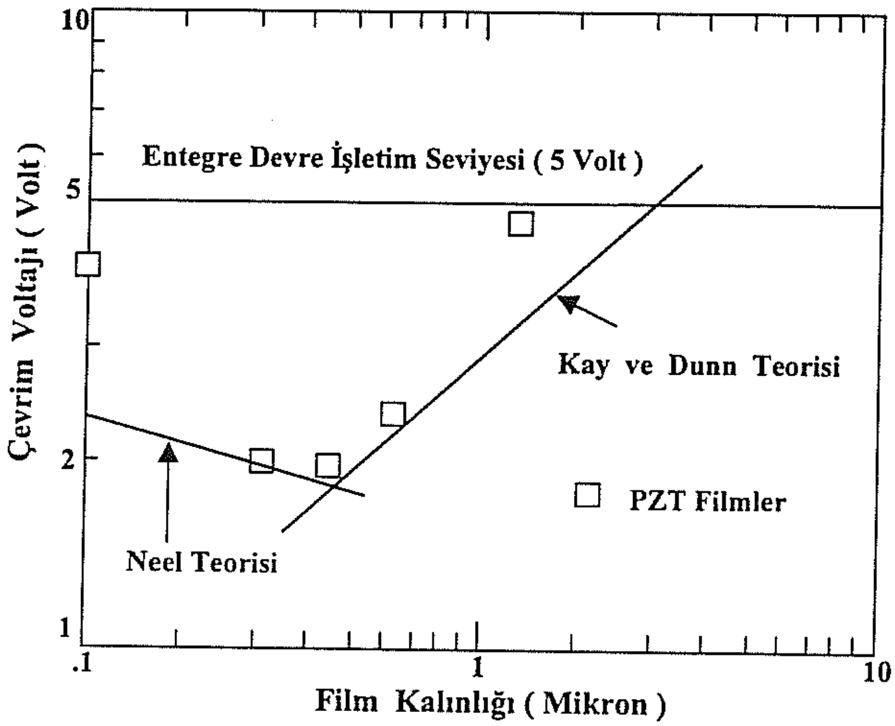


Şekil 2.3. Ferroelektrik PZT sisteminin tetragonal perovskit yapısı.



Şekil 2.4. $PbTiO_3$-$PbZrO_3$ faz diyagramı.

Ferroelektrik özellikleri nedeniyle PZT sisteminin neden çalışıldığı daha önceki bölümlerde verilmişti. Fakat neden ince film olarak bu çalışmaların ağırlık kazandığı ise Şekil 2.5 ile izah edilebilir. Bir ferroelektrik malzemenin polarizasyon durumunu tersine çevirmek için gerekli olan voltaj malzemenin kalınlığına bağlıdır ve malzemenin kalınlığı ile birlikte azalmaktadır. Bir ferroelektrik malzemeyi entegre devrelerde verimli olarak kullanabilmek için gerekli çevirme voltajı (switching voltage) 5 volttan daha az olmalıdır ve bu voltaj değerini elde edebilmek için gerekli olan film kalınlığı da 1 mikrondan daha az olmalıdır. Şekil 2.5'te çevirme voltajı film kalınlığına karşı verilmektedir. Kay ve Dunn teorisine göre çevirme voltajı $d^{2/3}$ ile (burada d film kalınlığını temsil etmektedir) doğru orantılı olarak değişmektedir. Şekilde görülebileceği gibi minimum çevirme voltajı 250 nanometre film kalınlığında elde edilmiştir. Hafiza uygulamalarında çok önemli olan çevirme hızı da (switching speed) film kalınlığı ile $d^{-2/3}$ orantısına bağlı kalarak değişmektedir.



Şekil 2.5. Ferroelektrik ince filmlerde çevirme voltajı-film kalınlığı değişimi.

2.3. Ferroelektrik Seramik İnce Filmlerin Özellikleri

i) **Piroelektrik özellikler :** PZT ve $PbTiO_3$ filmler hakkında şimdiye kadar yayınlanan değerler kütlesel seramiklerle aynı orandadır.

ii) **Piezoelektrik özellikler :** PZT filmler için d33, d31, k33, k31 ve kp piezoelektrik katsayıları sırasıyla 220 pC/N, -88 pC/N, 0.49, 0.22 ve 0.32 olarak rapor edilmiştir. Bu değerler kütlesel PZT seramiklerle aynı orandadır.

iii) **Optik özellikler :** Lityum niobat, KTN ve tungsten bronz ince filmler dalga yönlendirici özelliklere sahiptirler.

iv) **Ferroelektrik özellikler :** Ferroelektrik seramik ince filmlerin pek çoğunda histeresis özellikleri tespit edilmiştir. Polarizasyon özellikleri de kütlesel seramiklere benzemekle beraber, kalıcı polarizasyonun daha düşük olduğu rapor edilmektedir. Koersiv alan değeri ise kütlesel seramiklerden yaklaşık olarak 10 kat daha fazladır. Bu gözlemlerin nedenleri olarak arayüzey reaksiyonları ve küçük tane boyu düşünülmekle birlikte, bu konuda yoğun araştırma yapılması gerekmektedir.

v) **Dielektrik özellikler :** Oda sıcaklığındaki dielektrik sabiti kütlesel seramiklerle aynı değerde olmasına rağmen, dielektrik kayıpları daha fazladır. 1 µm'lik filmler için 1MV/cm değerinde bir dielektrik dayancı tesbit edilmiştir.

vi) **Radyasyon özellikleri :** PZT filmlerin 5 MRad doz altında ve 10^{11} Rad/sn hızında çok az bozulduklan gözlemlenmiştir.

2.4. Ferroelektrik Filmlerin Uygulama Alanları

i) **Hafıza uygulamaları :**

- Si üzerine kaplanan PZT filmler kullanılarak yapılan Ferroelektrik (FE) RAM malzemeler National Semiconductors ve Reytheon and Ramtron firmalarınca üretilmektedir. GaAs üzerine kaplanan PZT RAM malzemeler de McDonnell Douglas firmasınca yapılmaktadır. Bu uygulamalardaki prensip ferroelektrik seramiklerin anahtar kapasitör olarak kullanılmaları ve kalıcı bir bellek oluşturmalarıdır.
- $SrTiO_3$ ve $Ba_xSr_{1-x}TiO_3$ kullanılarak yapılan DRAM malzemeler ise NEC ve IBM firmalarınca geliştirilmektedir.
- $BaMgF_4$ filmler kullanılarak Westinghouse firması tarafından FE-FET malzemeler de üretilmiştir.

ii) **Piezoelektrik uygulamalar :** 100-200 rpm rotasyon hızları ve pN-m/V^2 mertebesinde normalize dönme momenti olan PZT mikromotorların çalışabildiği gösterilmiştir. Ayrıca $PbTiO_3$ film kullanılarak akustik mikroskop mercekleri ile koaksiyel ultrasonik transdüserler de yapılmaktadır.

iii) **Enfrarüj Uygulamaları :** Enfrarüj uygulamalar amacıyla, bolometrik tipi ince film ferroelektrik detektörler üzerinde çalışılmakta ve CCD devrelerin entegre kapasitör elemanları olarak kullanılmaları düşünülmektedir.

iv) **Akusto-optik ve elektro-optik uygulamalar :** PLZT ve PZT ince filmler kullanılarak yapılan akusto-optik ve elektro-optik elemanlar uygulamada kullanılmaktadırlar.

Tablo 1'de bazı ferroelektrik film sistemlerinde kullanılan malzemeler ile bu malzemelerin özellikleri ve uygulama alanları verilmektedir (Xu ve Mackenzie, 1992).

2.5. Üretim Teknikleri

Ferroelektrik ince filmlerin üretimi için RF sputter, metal organik kimyasal buhar depolaması, sol-jel vb.çeşitli yöntemler kullanılmaktadır. Bu metodlardan bazıları hakkında bilgiler aşağıdaki bölümlerde verilmektedir (Gurkovich ve Blum, 1985, Blum ve Gurkovich, 1985, Budd, 1986, Dey, et. al., 1987). Ayrıca Tablo 2'de bu yöntemlerden bazıları ve kullanıldıkları sistemler yer almaktadır.

i) **Çöktürme yöntemi :** Literatürde başlica iki tür çöktürme yöntemi ince filmlerin elde edilmesinde kullanılmaktadır : yaş metodlar ve vakum tekniği. Yaş metodlar arasinda karmaşık alkoksitler kullanılarak yapılan sol-jel tekniği ile molekül ağırlığı fazla olan çözeltiler (precursor) kullanılarak yapılan MOD teknikleri başta gelmektedir. En çok kullanılan vakum teknikleri ise reaktif püskürtme (ion beam assisted deposition, rf-diode veya magnetron sputtering), lazer püskürtme ve MOCVD yöntemleridir. MOCVD yöntemi daha kararlı ince filmler üretilmesini mümkün kılan bir teknik olmakla beraber, kullanılan çözeltilerin toksisite miktarı çok fazladır. Sol-jel teknigi düz yüzeylere rahatlıkla uygulanabilmesi nedeniyle tercih edilmektedir. Vakum teknikleri ile yaş teknikler kullanılarak elde edilen filmlerin performansı birbirlerine çok yakın olmakla beraber, mikroyapıların değişik olmasından kaynaklanan bazı farklardan söz edilebilir.

ii) **Elektrot yöntemi :** Bu yöntemde en çok karşılaşılan problemler film ve elektrot arasındaki yayınım, arayüzeyde oluşan hata yığılması ve yine arayüzeyde meydana gelen elektrokimyasal bozulmadır. En çok kullanılan elektrotlar Pt-Ti uçlu olanlardır. Bu yöntem üzerinde yapılan teorik ve deneysel çalışmalar yeterli değildir.

Tablo 1. Bazı ferroelektrik film sistemlerinde kullanılan malzemeler ile bu malzemelerin özellikleri ve uygulama alanları.

PEROVSKİT		
$BaTiO_3$	Dielektrik	Kapasitör, sensör, faz değiştirici
$SrTiO_3$	Piroelektrik	Piro-dedektör
PT	PTCR Piroelektrik Piezoelektrik	Termistör Piro-dedektör Akustik transdüser
PZT	Dielektrik Piroelektrik Piezoelektrik Elektrooptik	Buharlaşmayan hafiza Piro-dedektör SAW Dalga yönlendiricisi
PLZT	Piroelektrik Elektro-optik	Pirodedektör Dalga yönlendiricisi Optik hafiza Ekran
NİOBATLAR		
PMN	Dielektrik	Kapasitör
PMN/PT	Elektro-optik	Dalga yönlendiricisi
LT	Elektro-optik	Dalga yönlendiricisi, Optik modülatör
KN	Elektro-optik	Dalga yönlendiricisi, holograf depolama
KTN	Piroelectrik Elektro-optik	Piro-dedektör Dalga yönlendiricisi
TUNGSTEN-BRONZ		
SBN	Dielektrik	Hafiza

Tablo 2. Ferroelektrik ince filmlerin üretiminde kullanılan bazı teknikler.

FERROELEKTRİK İNCE FİLMLER		
Fiziksel teknikler		
Buharlaştırma	Püskürtme	Sıvı faz epitaksisi
$BaTiO_3$ $PbTiO_3$ PZT $Ba_4Ti_3O_{12}$ $BaMgF_4$ SbSI	$BaTiO_3$ $PbTiO_3$ PLZT PZT $KNbO_3$ $LiNbO_3$ $LiTaO_3$	$LiNbO_3$ $LiTaO_3$ KTN
Kimyasal teknikler		
Kimyasal buhar çöktürme	Metalorganik çöktürme	Sol-Jel
$PbTiO_3$ PZT $Pb(Sc_{0.5}Ta_{0.5})O_3$	$PbTiO_3$ PZT PLZT	PZT PLZT PMN KTN $KNbO_3$ $BaTiO_3$ $LiNbO_3$ SBN PBN

iii) **Yoğunlaştırma, kristalleştirme ve ısıl işlem yöntemi :** Isıl işlem genellikle 500°C'nin üzerinde yapılmaktadır. Bu işlemin çok hızlı olması, en az zarar açısından tercih edilmektedir. Isıl işlem sıcaklığı ve zamanının daha da düşürülebilmesi için çalışmalar yapılmaktadır.

Sol-jel prosesi ferroelektrik ince film üretiminde yeni bir yöntemdir (Yi, et. al., 1988, Reaney, et. al., 1994, Liu ve Phule, 1997, Carim, et. al., 1991, Barrow, et. al., 1997). Bu üretim tekniğinin avantajları şöyle sıralanabilir :

- Kimyasal kompozisyonun kolay kontrol edilebilmesi
- Homojen yapı
- Altlık üzerinde düzgün film yüzeyi
- Ucuz ekipman
- Daha kısa sürede üretim yapabilme
- Daha düşük üretim sıcaklıkları

2.6. Günümüzde Endüstriyel Durum

Ferroelektrik ince filmleri devre elemanı ve cihaz olarak üretebilecek iki tip endüstri mevcuttur.

- Mikroelektronik alandaki büyük endüstriler (Siemens, GEC, Thomson, Phillips gibi),
- Özel tipteki endüstriler (sensor veya mikromekanik elemanlar üreten endüstriler gibi).

Mikroelektronik alandaki en geniş uygulama yeri bellek malzemeleri ve ferroelektrik filmlerin DRAM, SRAM, EPROM ve ID-Card'lardaki kullanımlarıdır. Potansiyel avantajlar ise yüksek depolama kapasitesi, hızlı hesaplama süreci ve sonsuz okuma/yazma zamanı olarak sıralanabilir. Bu sahadaki diğer bir uygulama yeri de çipler üzerinde ince film olarak kaplanan ferroelektrik kapasitörlerdir (yüksek frekans tekkatman veya çok katmanlı kapasitörler).

Sensör alanındaki en yaygın uygulamalar ise kuvvet, ivme ve IR izleme olarak görülmektedir. Buradaki avantaj Si devrelerdeki sensör fonksiyonlarının doğrudan entegrasyonudur. Entegre frekans filtreleri ve mikro pompaların kullanımı da analitik enstrümantasyon alanında yeni uygulama sahalarına yol açabilecek gibi görünmektedir (tünel ve atomik mikroskop gibi).

BÖLÜM III

ÇALIŞMADA KULLANILAN DENEYSEL TEKNİKLER

3.1. Üretim Yöntemi

Tek boyutlu (uniform) ve kimyasal açıdan homojen olan ferroelektrik seramik (PZT, PLZT, $BaTiO_3$, $PbTiO_3$, $Sr_2Nb_2O_7$, $Ca_2Nb_2O_7$, $Sr_{0.5}Ba_{0.5}Nb_2O_6$, vb.) parçacıkların sol-gel/alkoksit, hidrotermal sentez ve birlikte çökeltme (co-precipitation) tekniğiyle hazırlanması ve sentezlenmesi konusundaki çalışmalar oldukça yenidir (Roy, et. al.,.1993, Payne, et. al., 1992, Bhalla, et. al., 1992).

Bu sistemdeki PZT ince filmlerin hazırlanmasında kullanılan alkoksitler, metal alkoksitler olup başlıcaları kurşun asetat trihidrat, titanyum izopropoksit, zirkonyum izopropoksit veya zirkonyum izobütoksittir. Bu alkoksitler ortamdaki neme karşı çok duyarlı olduklarından, bu oksitlerle yapılacak ferroelektrik film üretimi aşırı kontrollü atmosferlerde ve dolayısıyla özel ortamlarda gerçekleştirilir. Kurşundan ve PZT solüsyonlarından elde edilen esterlerin sistemden uzaklaştırılması için genellikle vakum yöntemi de dahil olmak üzere çok aşamalı distilasyon işlemleri kullanılır. Bu nedenle projemizde ferroelektrik film üretimi için söz konusu yöntem seçilmemiştir.

PZT seramik tozlarının Pechini yöntemi ile sitrat solüsyonlarından üretimi de literatürde çalışılmış yöntemlerden biridir (Pechini, 1967, Varela, et. al., 1992). Fakat bu yöntemde sentezleme işlemi sırasında oluşan polyester rezinin, organik kalıntıların yok edilmesi amacıyla, 800°C'ye kadar ısıtılması gerekmektedir. Dolayısı ile organik kalıntıların giderilmesi sonucu oluşacak fazın saflığını tayin edebilmek amacıyla XRD dışında, FTIR ve TGA gibi cihazların da kullanılması gündeme gelmektedir.

Kurşun baryum titanat tozlarının sentezinde kullanılan okzalat metodu da baryum ve kurşun titanatların amonyum titanil okzalat ile reaksiyonu neticesinde yüksek saflıkta, küçük taneli ve tek fazlı titanatları vermektedir. Bu yöntemde de okzalatların oksitlere dönüşümünü kontrol edebilmek amacıyla üretim sürecinin IR spektroskopisi gibi cihazlarla kontrol edilmesi gerekmektedir (Bowen, et. al., 1993).

A. Safari tarafından uygulanan birlikte çökeltme (coprecipitation) yönteminde ise Pb, Ba gibi metallerin nitratları ile $TiCl_4$'ün hidrojen peroksit ortamında 65°C gibi düşük sıcaklıklarda titrasyonu kullanılmaktadır (Safari, et. al., 1988). Ayrıca $ZrCl_4$ ve $Pb(NO_3)_2$ gibi solüsyonların EDTA solüsyonuna oda sıcaklığında eklenmesi ile de uygun bir "jel" elde etmek ve bu karışımı 80°C'de 24 saat süre ile ısıtarak istenen seramik tozları oluşturmakta mümkündür (Sale, et. al., 1992). Fakat bu yöntemlerle elde edilen seramik tozlar homojen boyutlarda olmamakta ve aglomere yapılar içermektedirler.

Yukarıda sözü edilen bu yöntemler ferroelektrik seramik filmlerin üretilmesinde bugüne kadar denenmiş olup, halen uygulamada kullanılmaktadırlar. Bu projede önerdiğimiz yöntem ise aglomere olmayan, ince tanecikli ve homojen boyuttaki PZT, PLZT ve benzeri ferroelektrik kompozisyondaki seramik tozların elde edilmesinde kullanılacak bir yöntemdir ve bu malzemeler için daha önceden kullanılmamıştır. Bu yöntemde üretilecek malzemede bulunması gereken katyonların nitrat, klorür veya asetatları üre $[(NH_2)_2CO]$ ortamında, 75-98°C sıcaklıkta yaklaşık 1 saat süre ile reaksiyona tabi tutulmaktadır. Burada ürenin kullanılmasındaki amaç amonyak eldesidir. Bu metodla üre ve yttrium tuzları (nitrat ve klorür) kullanılarak küresel, homojen boyutta yttrium oksit tozları ile üre ve Y-Al nitratları kullanılarak $Y_3Al_5O_{12}$ tozları başarıyla elde edilmişlerdir. Ayrıca aynı yöntemle $GdAlO_3$, $LaAlO_3$ ve $GdAl_{11}O_8$ tozlarının üretimi de yapılmıştır (Akınç, et. al., 1988).

Ferroelektrik kompozisyondaki $Pb(Zr,Ti)O_3$ filmlerin ve tozların üretimi için seçilen başlangıç malzemeleri aşağıda verilmektedir :

- $ZrCl_4$
- $TiCl_4$
- $PbCl_2$
- Üre $[(NH_2)_2CO]$

Bu klorürler kullanılarak hazırlanan stok çözeltilerin konsantrasyonları aşağıdaki gibidir.

Pb^{+2}	0.03 - 0.05 M
Zr^{+4}	0.4 M
Ti^{+4}	9.11 M
Üre	0.01 - 0.05 M

Deneyler sırasında kullanılan hesaplamalardan bir örnek aşağıdaki Tablo 3'de verilmektedir.

Tablo 3. Deneyler sırasında kullanılan hesaplamalardan bir örnek.

Atom Ağırlığı (gr/mole)	278.106	233.032	189.712
Çözelti	$PbCl_2$	$ZrCl_4$	$TiCl_4$ (1730gr/lt)
Çözelti (lt)	1.0	0.1	1.0
Çözelti (M)	0.0396	0.4	9.1191
Çözelti (gr)	11.0000	9.3213	-

Deneysel işlem basamakları :

- Stok çözeltilerden $Pb(Zr,Ti)O_3$ kompozisyonunu elde edecek miktarlarda alınan nümunelerin saf suda çözülmeleri.
- Çözeltilerin pH değerlerinin amonyum hidroksit ile kontrol edilmesi.
- Başlangıçta 0 ile 1 arasında değişen pH değerlerinin, amonyum hidroksit ilavesi ile jel elde edilirken 4.5-5.5 değerlerine ulaşması.
- Jel eldesi için çözeltinin 90-95°C'de 7-10 saat süreyle manyetik yolla karıştırılması.
- Bu işlemin çeşitli aşamalarında daldırma yöntemi ile silisyum ve Al_2O_3 altlıklar üzerinde filmlerin oluşturulması.
- Filmlere uygulanacak ısıl işlem şartlarının jellerin DTA ile yapılan termal karakterizasyonu neticesinde tesbit edilmesi.
- Filmlerin önce 150°C'de 1-2 saat süre ile kurutulmaları.
- Daha sonra oksijen atmosferinde 850°C'de 5 saat süreyle alümina potalar içerisinde ısıl işleme tabi tutulmaları.
- Isıtma ve soğutma hızlarının 20°C/dakika ile 1.5°C/dakika olarak uygulanmaları.
- Filmlerin ortalama olarak 1.1 ve 1.2 μm civarında bir kalınlıkta elde edilmesi (Tek bir kaplama işleminde elde edilen film 0.2 μm kalınlığında olmakta ve istenen kalınlık için kaplama işlemi bir çok kez tekrar edilmektedir).
- Film yüzeyleri, film kalınlığı, partikül boyutu gibi karakterizasyon işlemlerinin SEM (Jeol - JSM 6400) kullanılarak yapılması ve elementel kompozisyon analizlerinin ise aynı mikroskoba bağlı EDS ünitesi yardımıyla gerçekleştirilmesi (Nümuneler Tarama Elektron Mikroskobunda

incelenmeden önce 25 nm Au-Pd alaşımı ile kaplanmaktadırlar. EDS analizlerinde görünen Au ve Pd maksimaları bu kaplama işleminden dolayı spektrumda yer almaktadır).

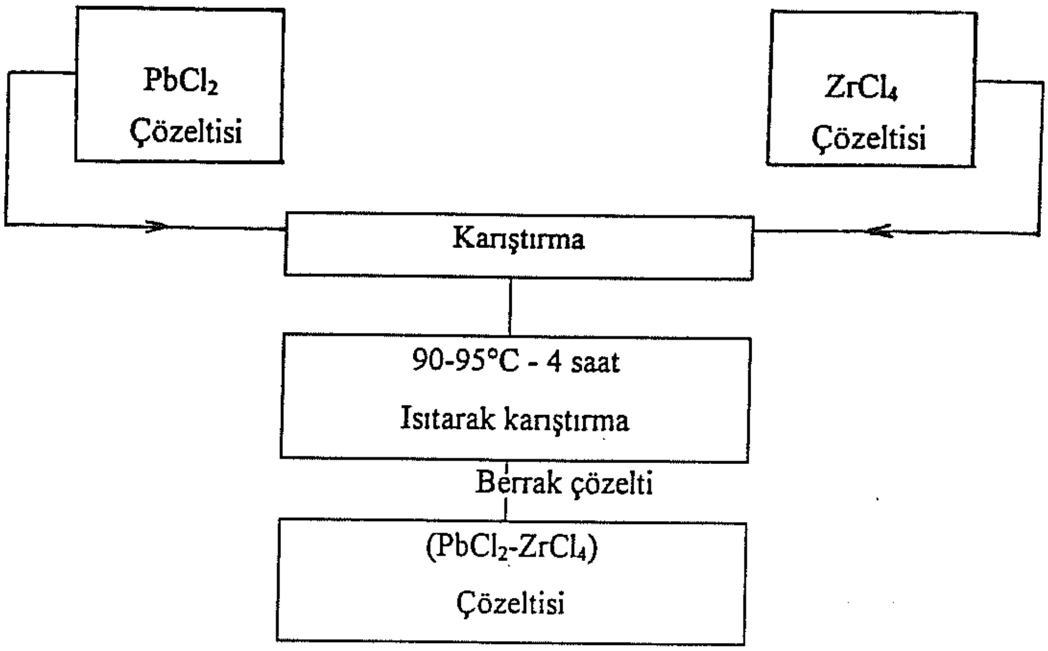
- Nümunelerin XRD işlemleri için Philips difraktometresinin kullanılması.

Hazırlanan çözeltilerden ayrıca tozlar (beyaz renkte) çöktürülerek 120°C'de 5-6 saat süreyle kurutulmuşlar ve 350°C'de 5 saat, 650°C'de 5 saat ve 850°C'de 5 saat oksijen atmosferinde ısıl işleme tabi tutulmuşlardır. Bu nümuneler XRD işlemleri için kullanılmışlardır. Aynı tozların SEM incelemeleri içinse çözeltilerden alınan örnekler SEM nümune tutucuları üzerinde önce kurutulmakta, daha sonra 25 nm Au-Pd alaşımı ile kaplanmaktadırlar. Tozların boyutları mikron altı seviyeye kadar indiğinden nümune tutucularının 0.5 μm'den daha az yüzey pürüzlülüğü değerlerine sahip olması gerekmektedir. Bu nedenle gerektiğinde nümune tutucuları ek parlatma işlemlerinden geçirilmektedir.

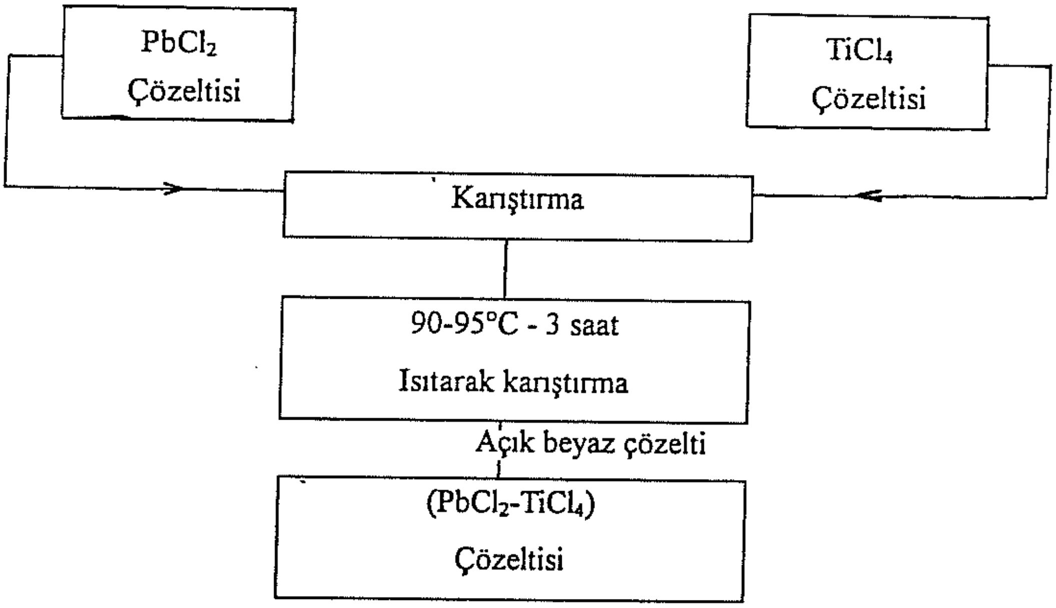
Ferroelektrik filmlerin ve tozların üretiminde kullanılan ve yukarıda ayrıntıları açıklanan yöntem şematik olarak aşağıda verilmektedir (Şekil 3.1-3.4).

3.2. XRD, SEM ve EDS Çalışmaları

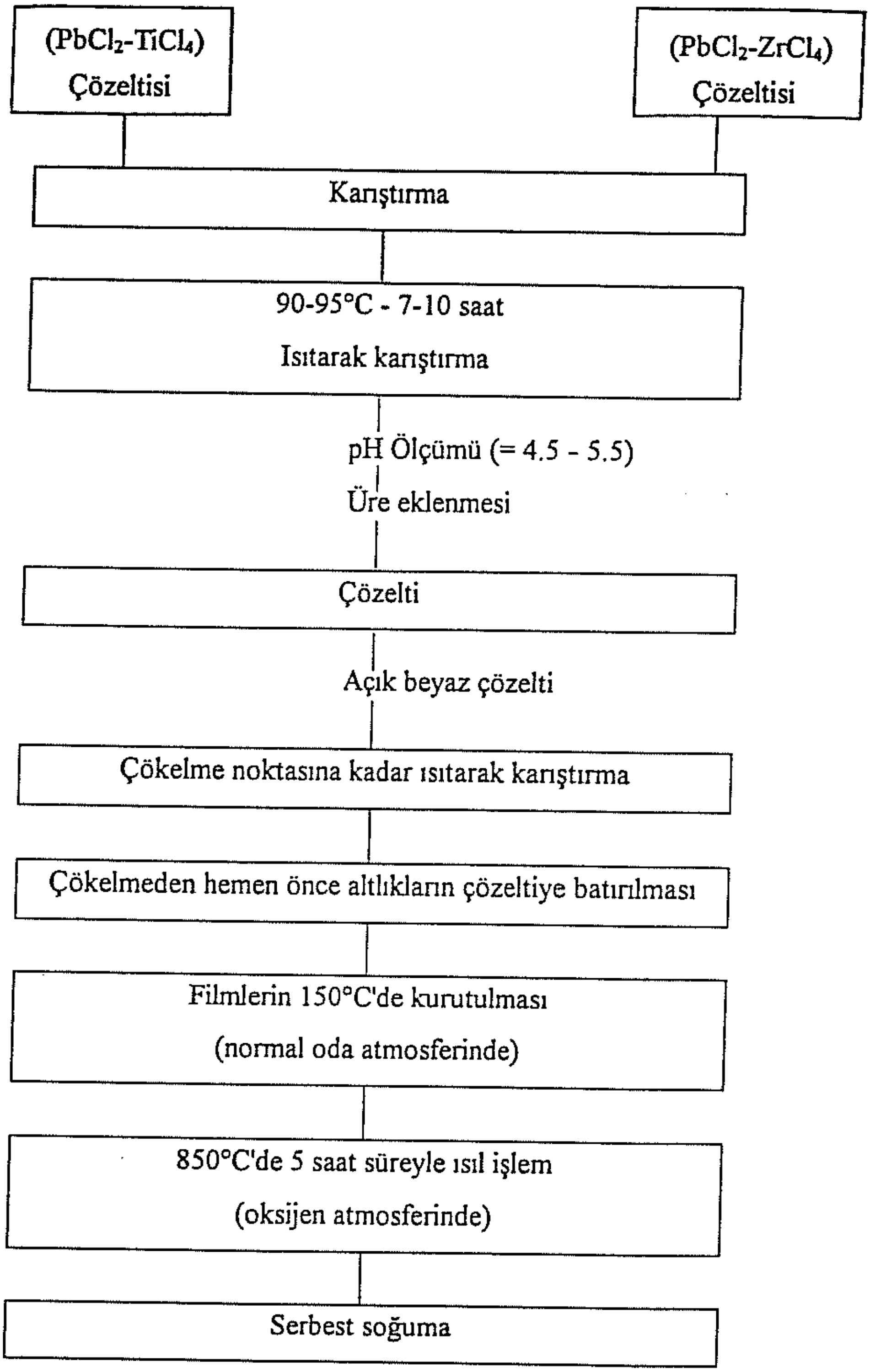
XRD çalışmaları Philips toz difraktometresinde Co Kα radyasyonu kullanılarak 20-90° aralığında yapılmıştır. Film yüzeyleri, film kalınlığı, partikül boyutu gibi karakterizasyon işlemleri SEM (Jeol - JSM 6400) kullanılarak yapılmış ve partiküllerin elementel kompozisyon analizleri ise aynı mikroskoba bağlı EDS ünitesi yardımıyla gerçekleştirilmiştir. Nümuneler Tarama Elektron Mikroskobu ile incelemeye alınmadan önce Microprep 300S PVD cihazında 25 nm altın-paladyum alaşımı ile kaplanmışlardır.



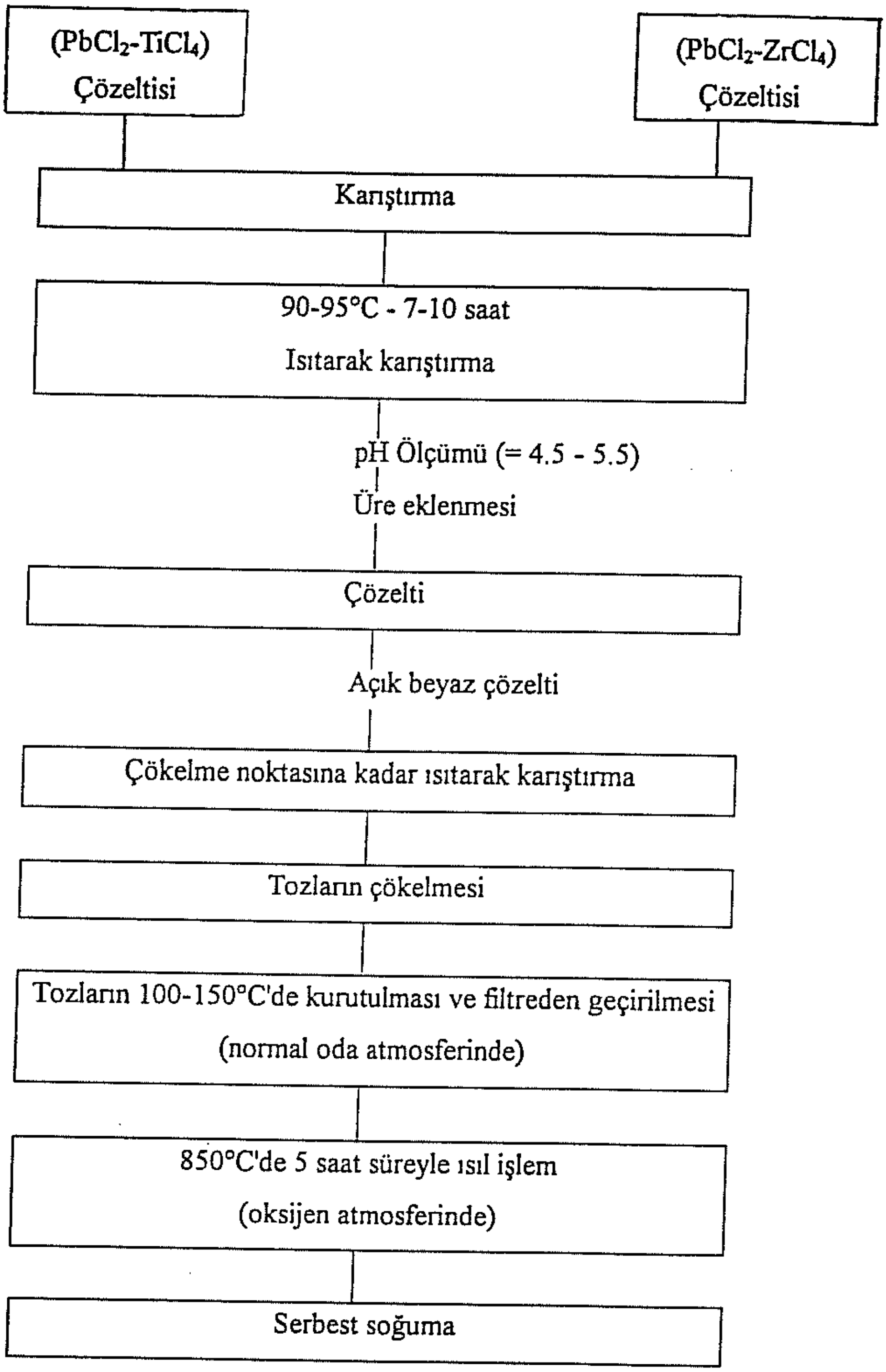
Şekil 3.1. ($PbCl_2$-$ZrCl_4$) çözeltisinin hazırlanması.



Şekil 3.2. ($PbCl_2$-$TiCl_4$) çözeltisinin hazırlanması.



Şekil 3.3. PZT filmlerin üretiminde kullanılan yöntem.



Şekil 3.4. PZT tozların üretiminde kullanılan yöntem.

3.3. Dielektrik Katsayısı ve Ferroelektrik Histeresis Döngüsü Ölçümleri

PZT kompozisyonundaki filmlerin dielektrik katsayıları kapasitans ölçümleri yapılarak bulunmuştur. Kapasitans ölçümleri 1 MHz sabit frekans değerinde HP 4194A Empedans/Kazanç Fazı Analiz Cihazı kullanılarak gerçekleştirilmiştir. Kapasitans ölçümleri için platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmler kullanılmıştır. Üre kullanılmadan elde edilen filmlerin yüzeyleri oldukça pürüzlü olduğundan ölçümler sağlıklı sonuçlar vermemiştir. Bunun nedeni olarakta bu filmlerdeki altlığa yapışmanın az olması nedeniyle oldukça gözenekli yapıda film eldesi olduğu düşünülmektedir. Kapasitans ölçümlerinden önce platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmlerin yüzeyinde gümüş kolloid boya yardımıyla iletken uçlar hazırlanmıştır.

PZT filmlerin ferroelektrik histeresis döngüsü ferroelektrik davranışı belirleyen parametreler olan artık polarizasyon (P_r) ve koersiv alan (E_c) değerlerini vermektedir. Bu histeresis döngüsünü tesbit etmek amacıyla standart Sawyer-Tower devresi kullanılarak polarizasyon histeresis döngüsü elde edilmiştir (Sawyer ve Tower, 1930). Bu ölçümlerde de yukarıdaki paragrafta açıklanan nedenlerden dolayı platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmler kullanılmıştır. İletken uçlar yine gümüş kolloid boya yardımıyla hazırlanmıştır. Sawyer-Tower devresi kullanılarak sayısal bir osiloskop yardımıyla X ve Y eksenleri boyunca voltaj değişimleri kaydedilmiş ve polarizasyon histeresis döngüsü elde edilmiştir.

BÖLÜM IV

SONUÇLAR VE TARTIŞMA

4.1. Tozların Sentezlenmesi

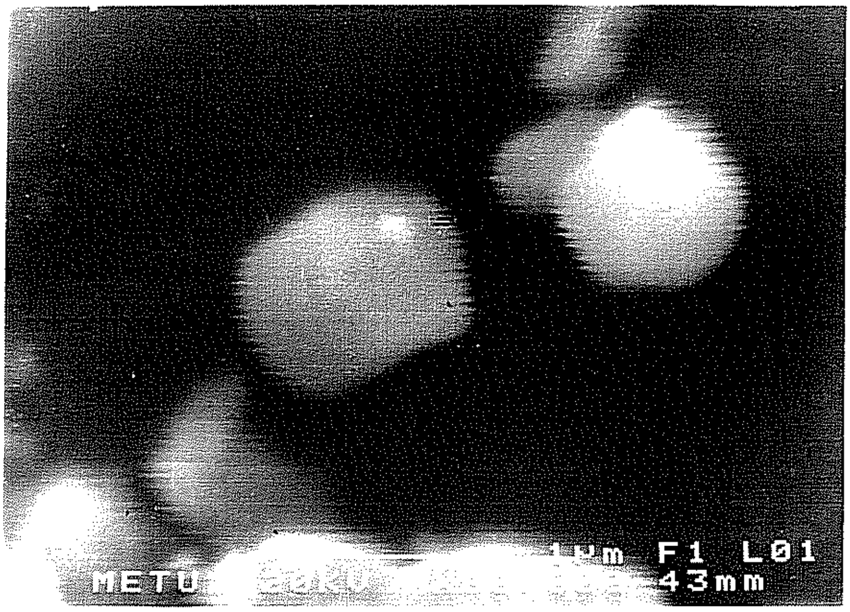
Şekil 4.1'de üre kullanılarak elde edilen PZT tozlarının SEM görüntüleri verilmektedir. Şekilden de görülebileceği gibi, üredeki ayrışım hızı çok düşük olduğundan, elde edilen tozların boyutları mikronaltı büyüklüklerden birkaç mikrona kadar değişmektedir. Buna karşılık üre kullanılmadan elde edilen aynı kompozisyondaki PZT tozlarının büyüklükleri ise 50 - 100 μm civarındadır (Şekil 4.2). Böylece üre kullanılarak yapılan homojen çökeltme işleminde mikron büyüklükte, homojen tozlar elde edilebildiği anlaşılmıştır.

Küçük boyutlu (mikron altı) ve homojen kompozisyondaki PZT tozlarının üretimi fiziksel özellikler açısından da son derece önemlidir. Tozların agglomere olarak daha büyük boyutlarda elde edilmesi veya tozlardaki kimyasal heterojenlik fiziksel özelliklerde istenen değerlerin elde edilememesine neden olmaktadır (Xu ve Mackenzie, 1992). Ayrıca mikron altı boyutlardaki tozlar kullanılarak üretilen PZT seramiklerde proses sıcaklıklarında olumlu oranda azalmalar görülmektedir.

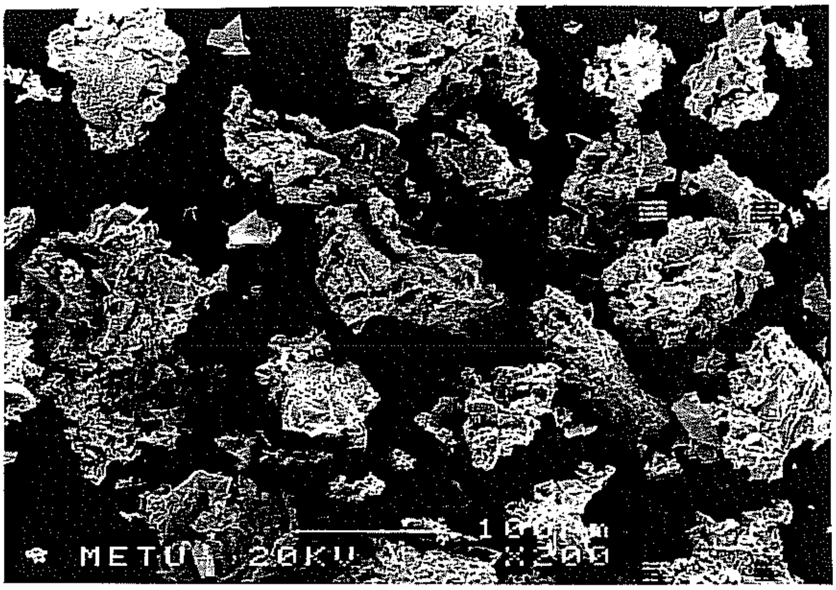
4.2. Kristalizasyon Sıcaklığının Tayini

PZT filmlerin ve tozların oksijen atmosferi içinde yapılan kristalizasyon işlemi XRD ile kontrol edilmektedir. Kristalizasyon 350°C civarında başlamakta, 650°C'de piroklor (pyrochlore) fazın miktarı azalmakta ve nihayet 850°C'de 5 saat ısıl işlem sonrasında nümune tamamiyle "perovskit" yapıyı göstermektedir. Bu sonuca ulaşabilmek amacıyla PZT tozlar ile bir seri deney yapılmış ve neticeler aşağıda verilen Tablo 4'te gösterilmektedir.

Tablo 4'te görüldüğü gibi tetragonal yapı artan sıcaklıkla birlikte XRD tepelerindeki tetragonal ayrışımın netleşmesinden de anlaşılabileceği üzere daha belirginleşmektedir. Yukarıda verilen 850°C ısıl işlem sıcaklığı, perovskit yapının tamamıyla belirdiği ve piroklor fazının görülmediği sıcaklık olarak tesbit edilmiş ve tüm çalışmada kristalizasyon için kullanılan ısıl işlem sıcaklığı olarak belirlenmiştir.



Şekil 4.1. Üre kullanılarak elde edilen PZT tozlarının SEM görüntüleri. Tane büyüklüğü 1 μm'den küçüktür.



Şekil 4.2. Üre kullanılmadan elde edilen PZT tozlarının SEM görüntüleri.

Tablo 4. PZT tozlara uygulanan ısıl işlemler ve XRD ile gözlemlenen fazlar.

Sıcaklık (°C)	Süre (saat)	Mevcut Fazlar
350°C	5	$PbTiO_3$, Piroklor, Perovskit, Tanımlanamayan fazlar
550°C	5	$PbTiO_3$, Piroklor, Perovskit
750°C	5	Piroklor,Perovskit
850°C	3	Piroklor,Perovskit
850°C	5	Perovskit

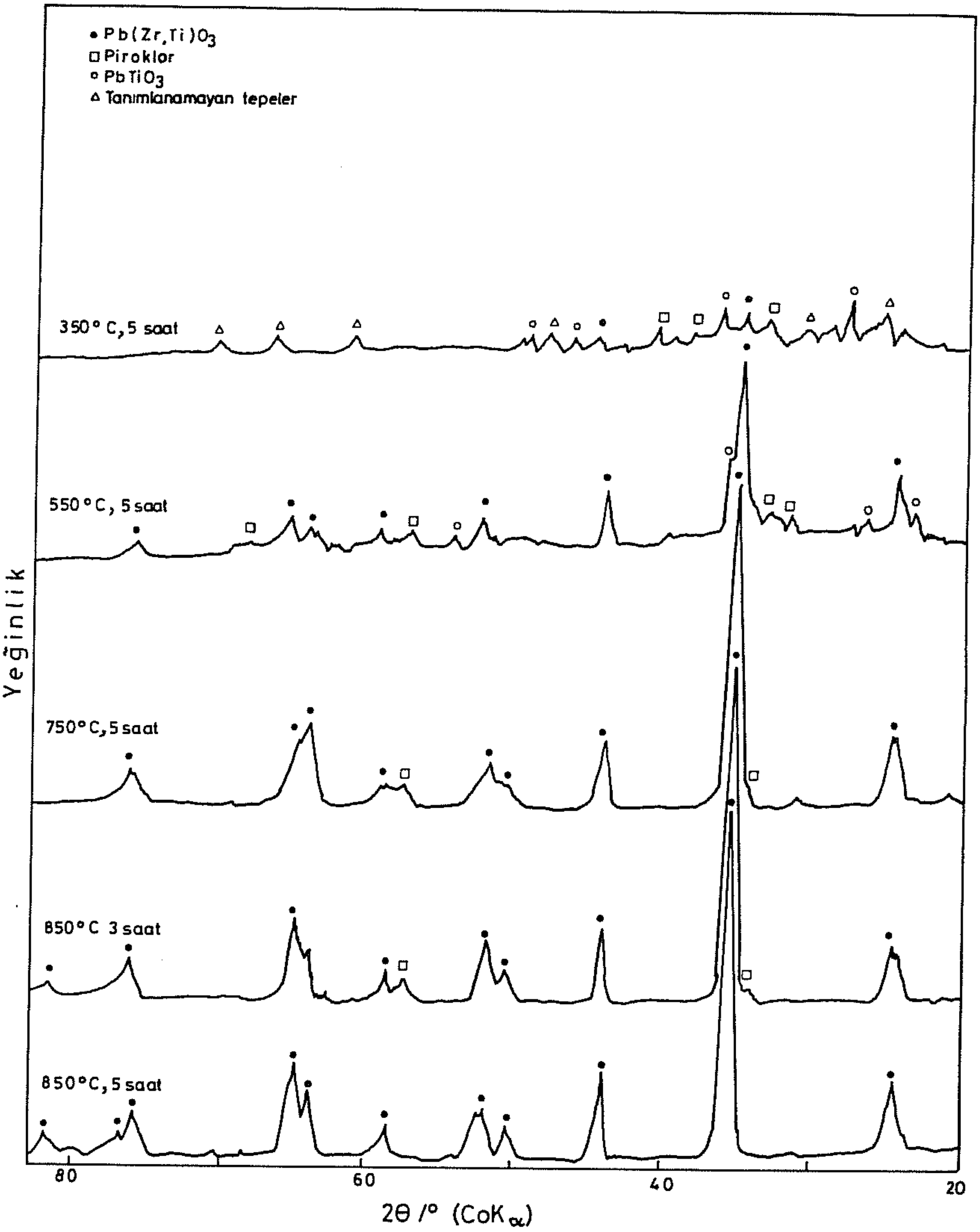
Diğer konvansiyonel metodlar oksitlerin 1200°C'de en az 2 saat süreyle sinterlenmesini gerektirmektedir ki, bu sıcaklıkta PbO uçuculuğu çok yüksektir. PZT tozlar ile yapılan bu işlemler neticesinde perovskit yapının tam olarak belirdiği ısıl işlem sıcaklığı olarak 850°C seçilmiş ve PZT filmlere de aynı ısıl işlem sıcaklığı uygulanmıştır. PZT tozlar ile gerçekleştirilen XRD çalışmalarının neticeleri toplu olarak Şekil 4.3'te verilmektedir. Aşağıdaki Tablo 5'te XRD (X-ışınları difraksiyonu) ile PZT filmlerde belirlenen fazlar yer almaktadır.

Tablo 5. PZT kompozisyonundaki filmlerde çeşitli sıcaklıklarda XRD ile belirlenen fazlar.

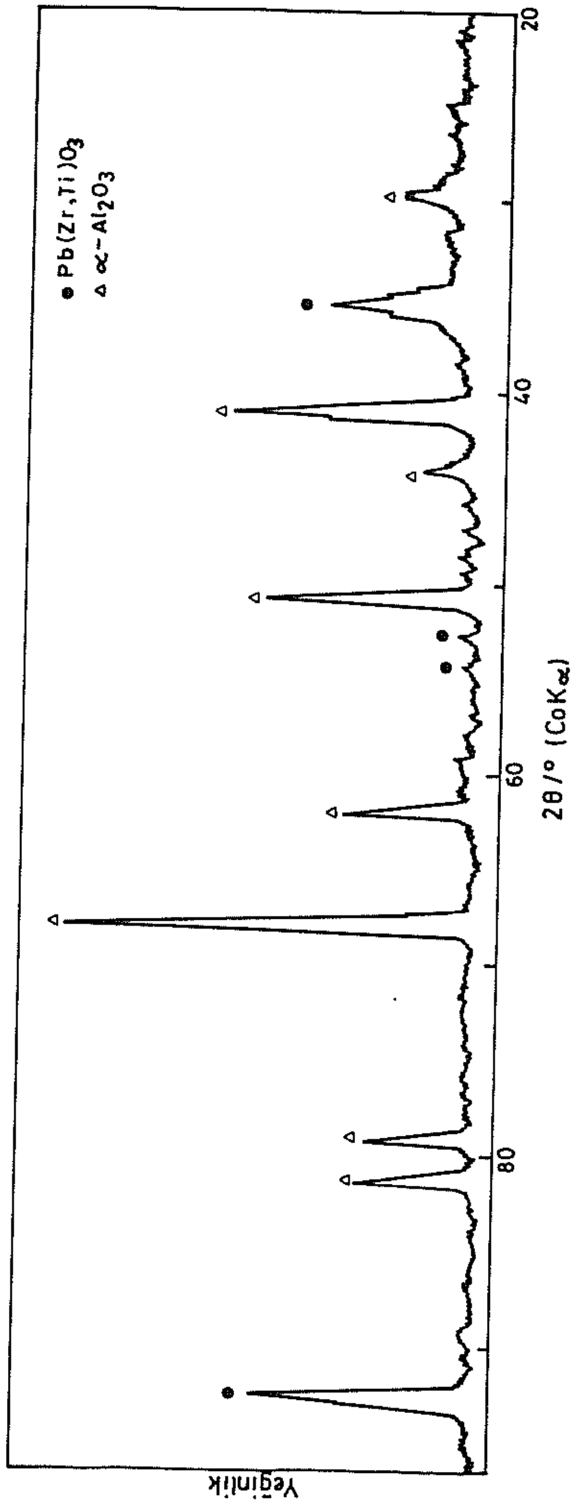
Sıcaklık	Fazlar
350°C	Piroklor, perovskit, altlık (Si veya Al_2O_3)
650°C	Piroklor, perovskit, altlık (Si veya Al_2O_3)
850°C	Perovskit, altlık (Si veya Al_2O_3)

Sol-jel yöntemi kullanılarak üretilen PZT ince filmlerde perovskit yapının görüldüğü ısıl işlem sıcaklığı tozlara göre yaklaşık 50°C daha fazla olarak belirlenmiştir. Bu sıcaklık film kalınlığı ve kompozisyonuna bağlı olarak değişmekle birlikte, genel olarak 800°C'nin üzerindedir. Şekil 4.4 ve 4.5 Al_2O_3 ve Si altlık üzerinde elde edilen PZT filmlerin 850°C'deki ısıl işlemlerinden sonra elde edilen XRD spektrumlarıdır. Bu spektrumlar polikristal altlıklar üzerine kaplanan filmlerden elde edildiğinden, filmlerde herhangi bir yönlenme görülmemektedir.

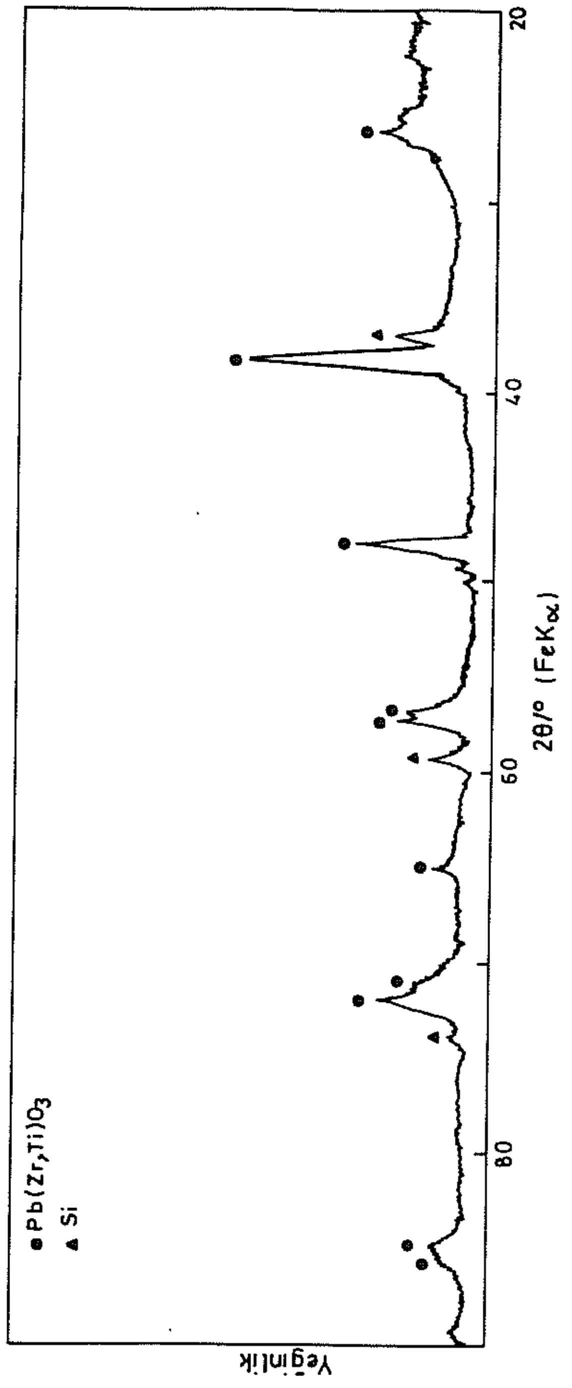
Jellerden elde edilen filmlerden alınan XRD spektrumlarının vermiş olduğu kafes parametreleri, sinterlenmiş nümunelerden elde edilen spektrumların verdiği kafes parametreleri ile uyum



Şekil 4.3. Pb(Zr,Ti)O$_3$ kompozisyonundaki tozların değişik derecelerdeki ısıl işlemleri neticesinde elde edilen XRD spektrumları.



Şekil 4.4. Al_2O_3 üzerinde elde edilen PZT filmin 850°C'de 5 saatlik ısıl işlem sonrasında elde edilen XRD spektrumu.



Şekil 4.5. Pt kaplanmış Si üzerinde elde edilen PZT filmin 850°C'de 5 saatlik ısıl işlem sonrasında elde edilen XRD spektrumu.

göstermektedir (a = 4.04 Å, c = 4.13 Å). Bu sonuç projede kullanılan yöntemle elde edilen filmlerin kimyasal kompozisyonunun konvansiyonel seramik üretim metodları ile elde edilen hacimsel (bulk) nümunelerle benzer olduğunu ortaya koymaktadır.

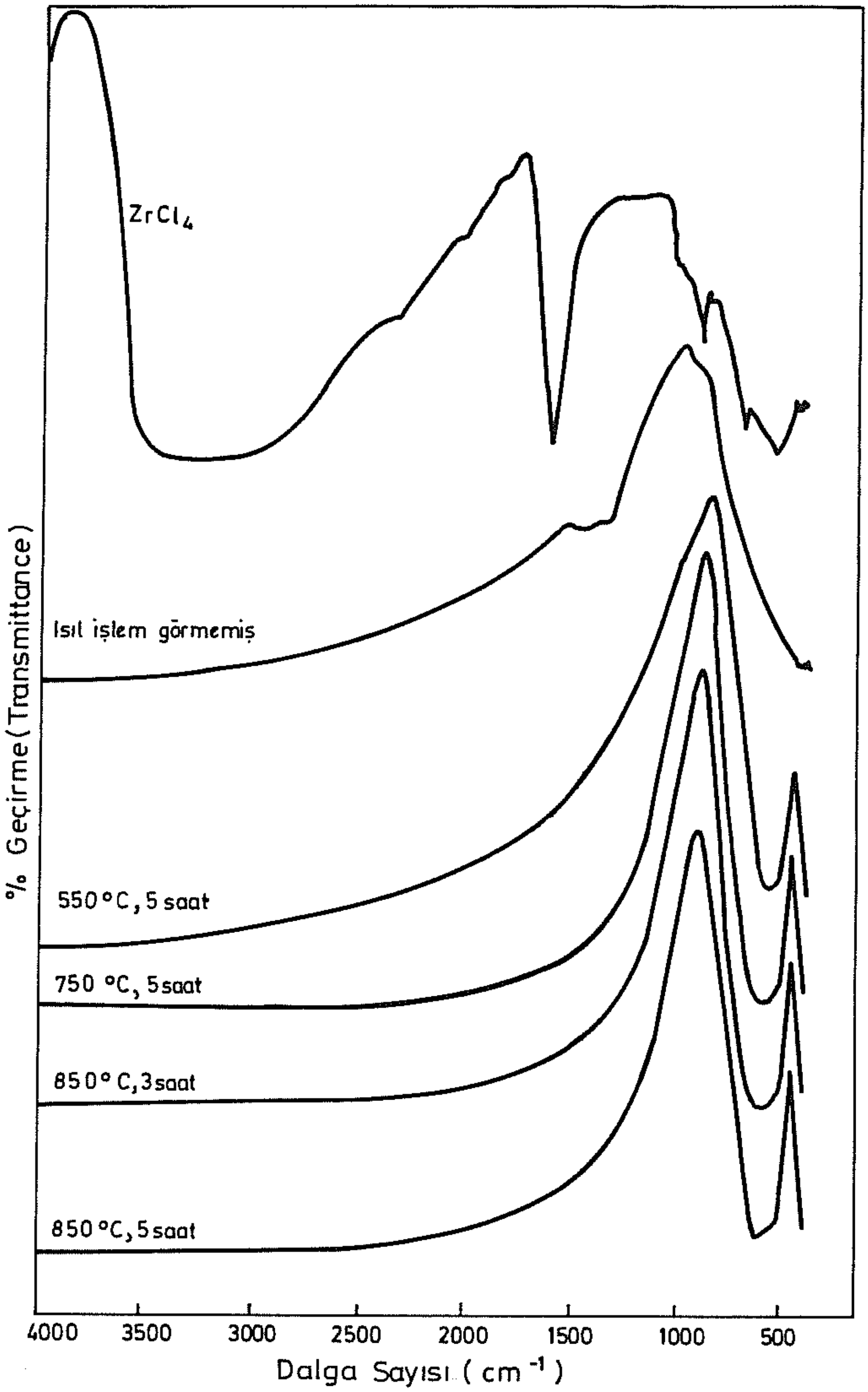
4.3. PZT Filmlerdeki Klor Miktarı

PZT tozların ve filmlerin elde edilmesinde başlangıç malzemeleri olarak klor içeren çözeltiler kullanıldığından, üretilen toz ve filmlerde ısıl işlem sonrası klor bulunup bulunmadığı ferroelektrik özellikler açısından önem taşımaktadır. Bu nedenle bütün toz ve film örneklerde EDS analizleri gerçekleştirilmiş ve 850°C'deki 5 saatlik ısıl işlemin her iki tür nümune için de yeterli olduğu anlaşılmıştır. XRD ve EDS analizleri neticesinde 850°C ısıl işlem sıcaklığı kristalizasyon için yeterli görünse de, her iki yöntemin limiti altında kalan çok küçük miktarlar için FTIR (Fourier Transform Infrared Spectroscopy) analizleri yapılarak seçilen ısıl işlem sıcaklığının (850°C) yeterli olup olmadığı test edilmiştir. FTIR neticeleri de örneklerde kalıntı klor bulunmadığını ve spektrumlardaki tepenin PZT kompozisyonundaki oksitlerin bir bileşimi olduğunu göstermektedir (Şekil 4.6).

EDS analizlerinin neticeleri Tablo 6'da verilmektedir. Bu tabloda görüldüğü gibi ısıl işlem görmeyen örneklerdeki EDS analizlerinde kullanılan çözeltilerden gelen Cl tepesi bulunurken, bu tepe ısıl işlem sonrasında ortadan kalkmaktadır (Şekil 4.7 ve Şekil 4.8). Fakat daha düşük sıcaklıklarda yapılan ısıl işlemlerden sonra Cl tepeleri yine görülmektedir (Şekil 4.9).

4.4. Filmlerdeki Elementlerin Homojen Dağılımı

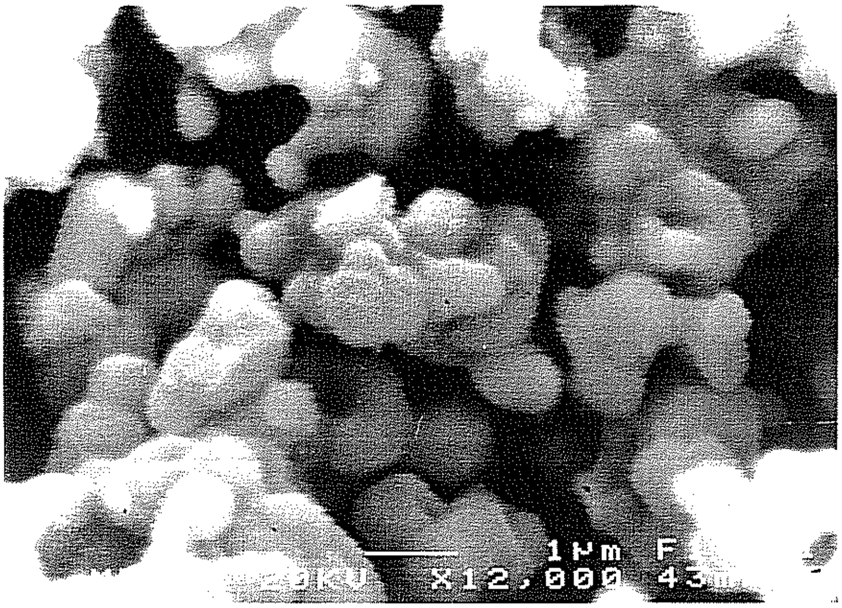
Projede en çok üzerinde durulan problemlerden biri de film elemanlarının homojen olarak dağılımını sağlamak olmuştur. Bu nedenle çözeltiler çeşitli sıcaklıklarda (<100°C) 24 saate varan sürelerde manyetik olarak karıştırılarak, hazırlanan filmlerin kompozisyonunun homojen olmasına çalışılmıştır. Şekil 4.10'da Al_2O_3 üzerinde elde edilen filmin ısıl işlem öncesi görüntüleri verilmektedir. Şekil 4.10'da verilen Tarama Elektron Mikroskobu görüntüsünde 1 ve 2 numara olarak işaretlenen bölgelerde kurşunca zengin ve fakir bölgeler yer almaktadır. Şekil 4.11'de ise aynı bölgelerin EDS spektrumları verilmiştir. Film ısıl işlem öncesi durumunda olduğundan Cl tepeleri de spektrumda yer almaktadır. Aynı filmin ısıl işlem sonrası elde edilen element dağılımı ise Şekil 4.12'de verilen X-ışınları haritasında görülmekte ve oldukça homojen bir dağılımı yansıtmaktadır.



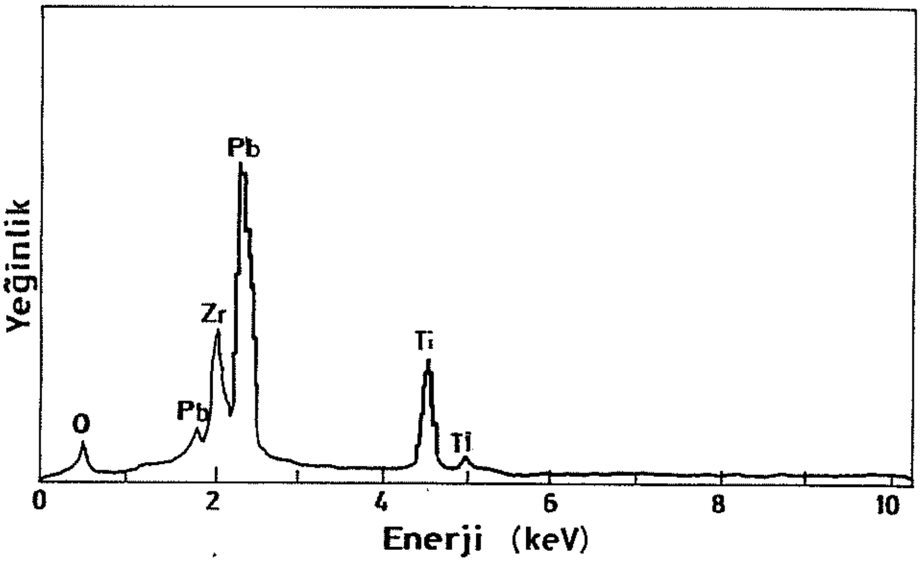
Şekil 4.6. $ZrCl_4$ ile ısıl işlem görmemiş ve değişik sıcaklıklarda ısıl işlem görmüş PZT tozların FTIR spektrumları.

Tablo 6. PZT toz ve filmleri üzerinde yapılan EDS analizlerinin neticeleri.

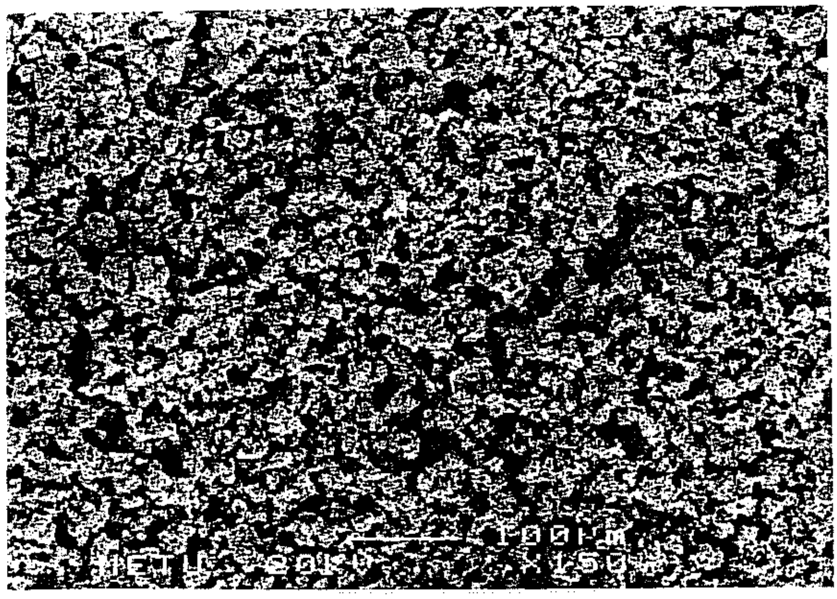
PZT Tozlar	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Oranı
Isıl işlem görmemiş	32.86	19.55	15.07	32.52	1:0.59:0.49
350°C, 5 saat	37.96	15.86	19.64	26.54	1:0.42:0.52
550°C, 5 saat	40.94	24.82	24.03	10.21	1:0.61:0.57
750°C, 5 saat	47.62	18.33	21.12	12.93	1:0.38:0.44
850°C, 3 saat	49.88	23.83	26.29	-	1:0.48:0.53
850°C, 5 saat	45.59	27.11	27.30	-	1:0.59:0.60
850°C, 5 saat(üre yok)	49.79	22.93	27.28	-	1:0.46:0.55
PZT Film/Al$_2$O$_3$ Altlık	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Oranı
Isıl işlem görmemiş	41.73	14.00	24.19	20.10	1:0.33:0.58
850°C, 3 saat	39.17	20.22	26.45	14.16	1:0.52:0.68
850°C, 5 saat	48.79	24.46	31.75	-	1:0.50:0.65
850°C, 5 saat (Ti-zengin faz)	21.71	27.89	50.41	-	1:1.28:2.32
850°C, 5 saat(üre yok)	38.79	30.28	30.93	-	1:0.78:0.80
PZT Film/Pt-kaplı Si	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Oranı
Isıl işlem görmemiş	44.66	14.73	22.01	18.60	1:0.33:0.49
850°C, 3 saat	35.79	28.94	22.81	12.46	1:0.81:0.64
850°C, 5 saat	42.61	24.96	32.43	-	1:0.59:0.76
850°C, 5 saat(üre yok)	42.74	27.19	30.07	-	1:0.64:0.70



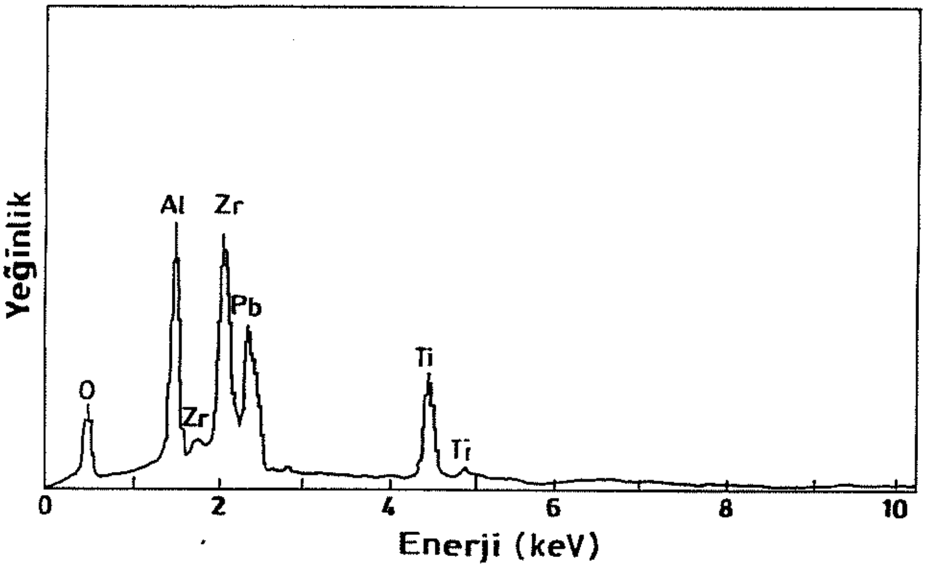
Şekil 4.7.a. Üre kullanılarak elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT tozların SEM görüntüsü.



Şekil 4.7.b. Üre kullanılarak elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT tozların EDS analizi.

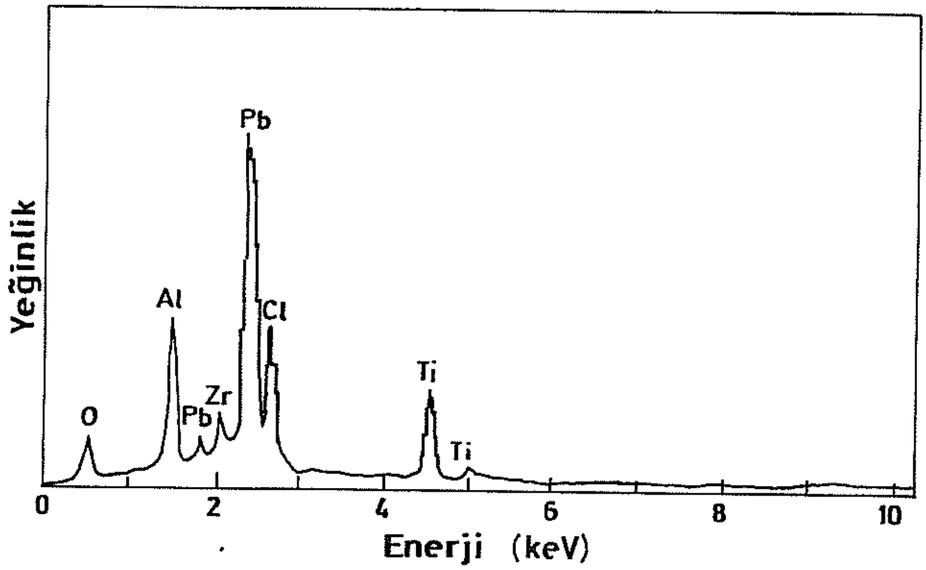


Şekil 4.8.a. Al_2O_3 altlık üzerinde üre kullanılarak elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT filmin SEM görüntüsü.

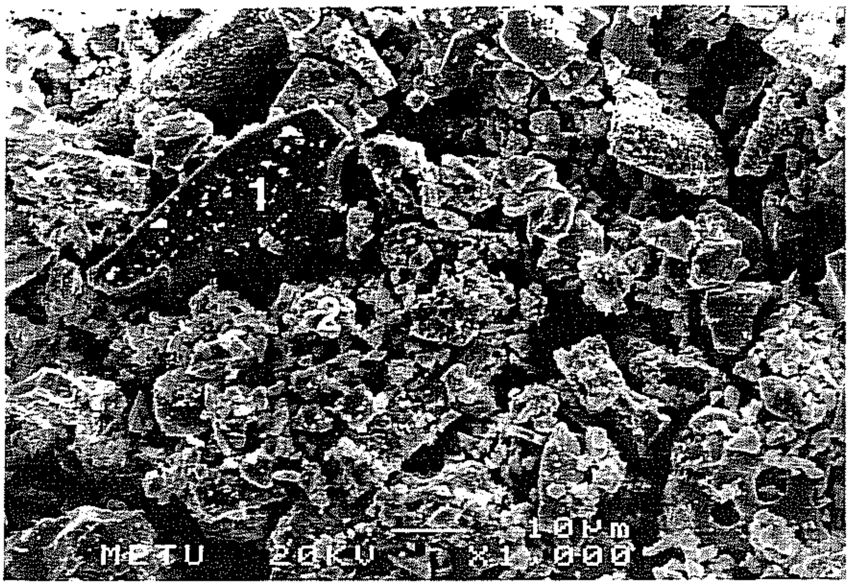


Şekil 4.8.b. Al_2O_3 altlık üzerinde üre kullanılarak elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT filmin EDS analizi.

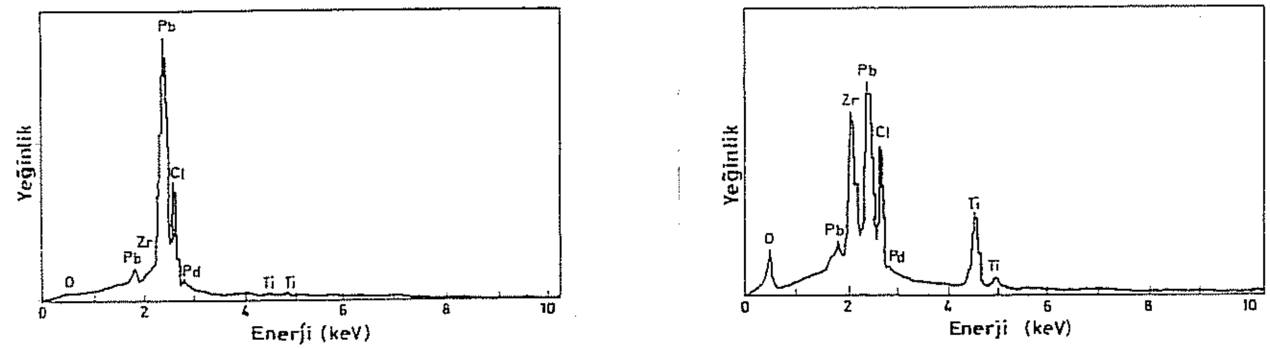
Şekil 4.9.a. Al_2O_3 altlık üzerinde üre kullanılmadan elde edilen ve ısıl işlem öncesi 150°C'de 2 saat süreyle kurutulan PZT filmin SEM görüntüsü.



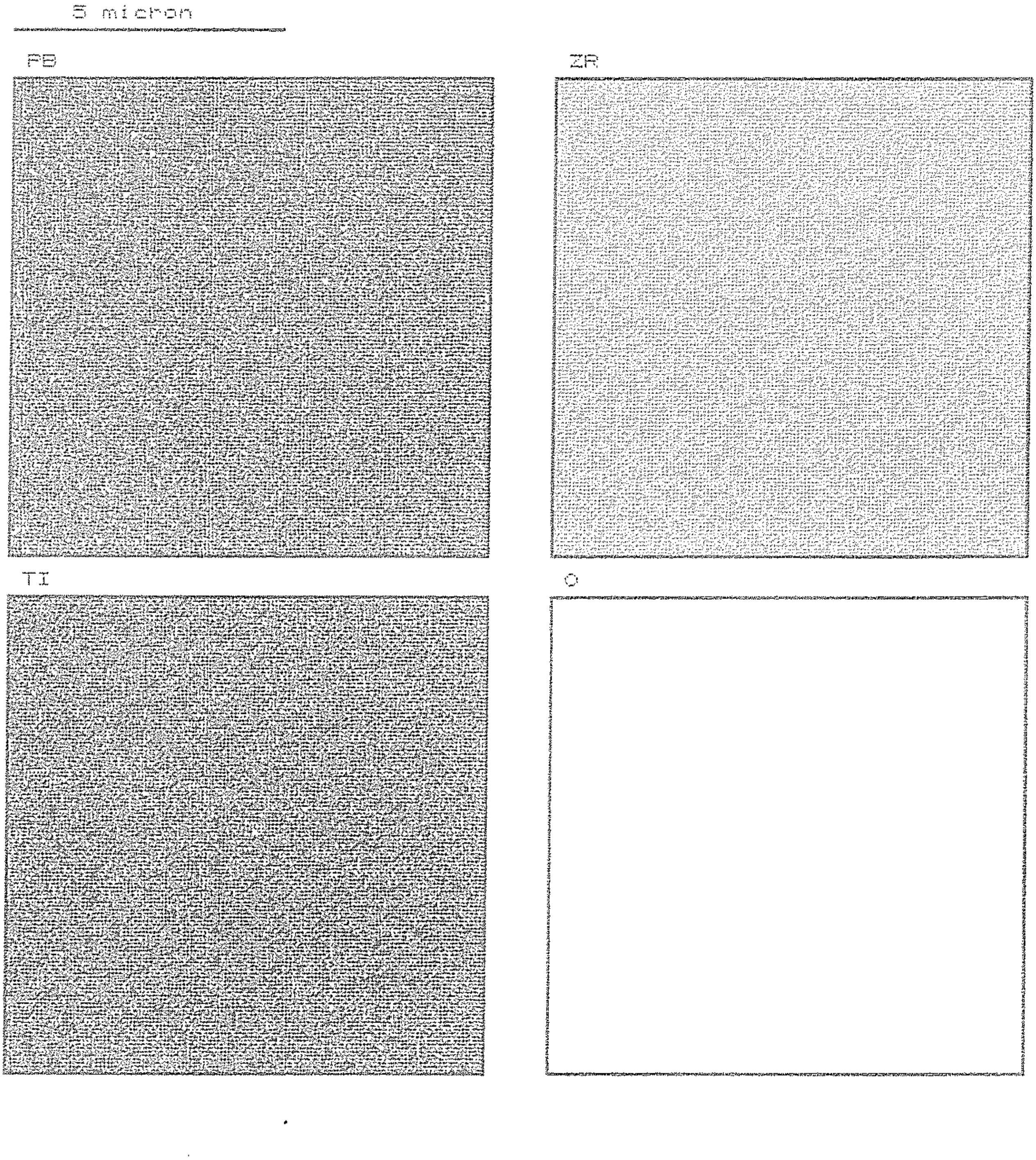
Şekil 4.9.b. Al_2O_3 altlık üzerinde üre kullanılmadan elde edilen ve 850°C'de 3 saat süreyle ısıl işleme tabi tutulan PZT filmin EDS analizi.



Şekil 4.10. Al_2O_3 altlık üzerinde üre kullanılarak elde edilen ve ısıl işlem öncesi 150°C'de 2 saat süreyle kurutulan PZT filmin SEM görüntüsü.



Şekil 4.11. Şekil 4.10'da verilen filmin üzerindeki 1 ve 2 noktalarından alınan EDS analizleri.



Şekil 4.12. Al_2O_3 altlık üzerinde üre kullanılarak elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT filmin X-ışınları haritası.

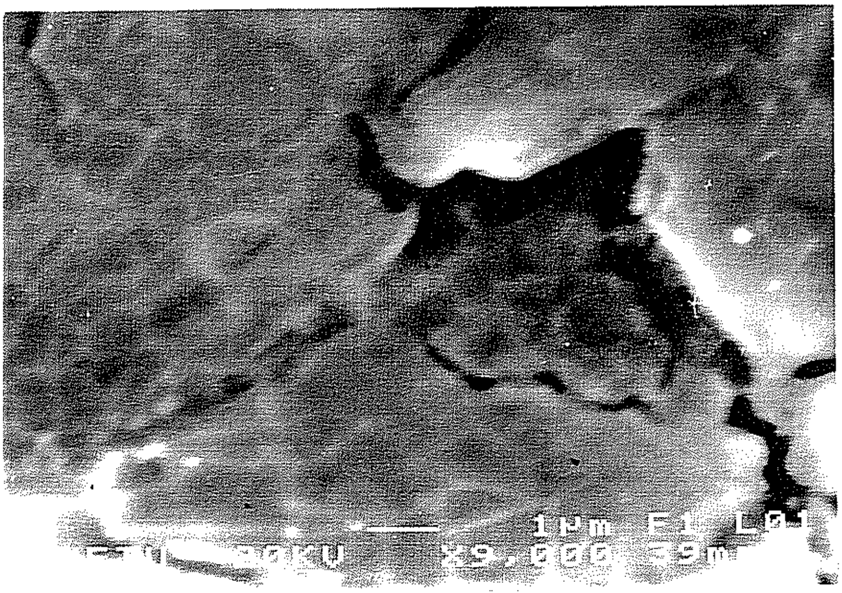
4.5. Filmlerin Taban Malzemesine Yapışkanlığı

Ferroelektrik filmlerin taban malzemesi olarak kullanılan alümina ve silisyuma olan yapışkanlığı uygulamadaki en önemli noktalardan biri olduğundan projede en çok üzerinde durulan konuların başında gelmektedir. Perovskit yapıya sahip olan PZT kompozisyonundaki film taban malzemesi olan alümina veya silisyumdan farklı kristal yapıya ve termal genleşme katsayısına sahip olduğundan yapışma mükemmel olmamakta ve yer yer dökülmeler görülebilmektedir. Fakat her iki taban malzemesi de uygulamada yoğun olarak kullanıldıklarından bu taban malzemeleri üzerine filmleri büyütme zorunluluk olarak ortaya çıkmaktadır. Literatürde her iki taban malzemesine alternatif olarak başka malzemelerde kullanılmasına rağmen elektronik sanayiindeki yaygın kullanımları nedeniyle bu iki malzeme halen en çok çalışılan altlıkların başında gelmektedirler.

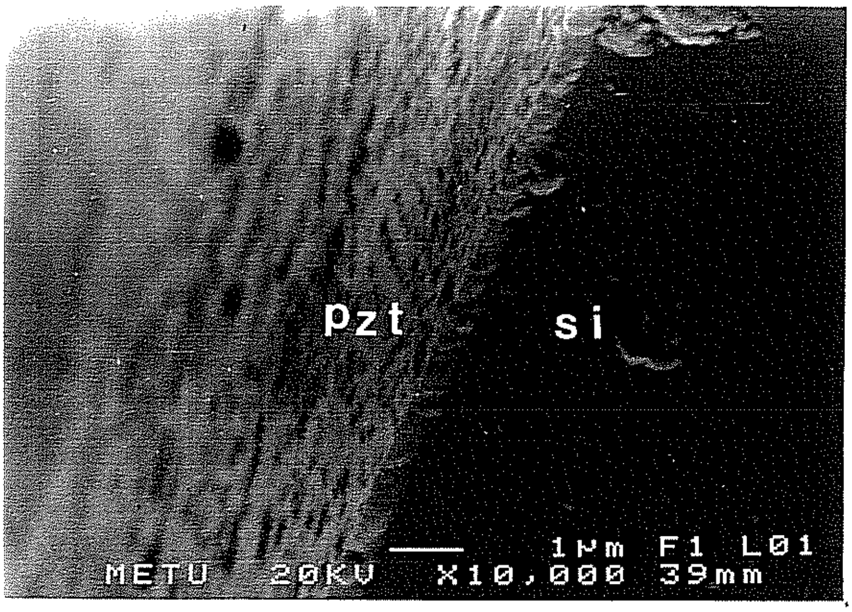
Projedeki çalışmalarda Si altlık üzerinde elde edilen filmin yüzeyinden alınan bir görüntü Şekil 4.13'te verilmektedir. Si altlık üzerine doğrudan kaplanan filmlerde diğer altlıklara oranla daha fazla çatlaklara rastlanmaktadır. Bu problemi azaltmak amacıyla silisyum yüzeyine film kaplanmadan önce bir tampon tabakası uygulanması en uygun çözüm olarak düşünülmüştür. Bu tampon tabaka ısıl işlem sıcaklıklarında tepkimeye girerek başka problemler yaratmaması için platin olarak seçilmiştir. Platin kaplanmış Si üzerinde elde edilen PZT filmlerdeki homojenlik ve kaplama yapışkanlığı bu seçimin doğru olduğunu göstermiştir (Şekil 4.14).

Ayrıca filmin eldesi için kullanılan jelin yoğunluğu organik katkı maddeleri (Metil selülöz veya polisitren gibi) ekleyerek arttırılmıştır. Böylece daha ince filmler elde edilebilmiş ve pek çok kez tekrar edilen daldırma-kurutma işlemleri asgariye indirilerek filmdeki çatlakların önüne geçilmiştir.

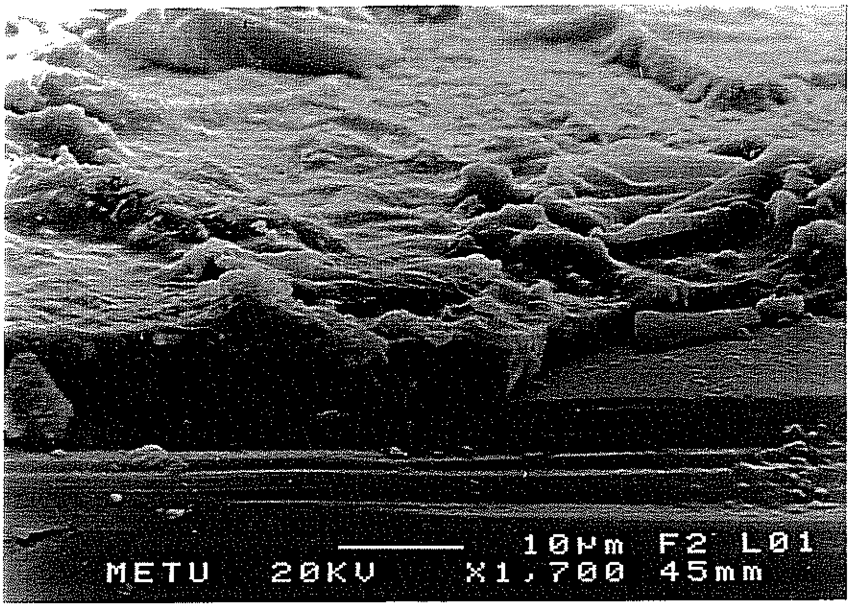
Ayrıca üre kullanılarak elde edilen çözeltilerden üretilen filmlerde yüzey daha düzgün ve altlığa yapışma daha fazla olarak belirlenmiştir. Bunun nedeni olarak üre kullanımı neticesinde elde edilen daha küçük ve homojen dağılımlı tozlar verilebilir. Bu neticeye örnek olarak verilen ve platin kaplanmış Si altlıklar üzerinde üre kullanılmadan elde edilen filmdeki yüzey pürüzlülüğünün (Şekil 4.15) üre kullanılarak elde edilen filme oranla çok daha fazla olduğu görülmektedir (Şekil 4.16). Şekil 4.16'da 1 numaralı bölge PZT filmi, 2 numaralı bölge ise Si altlığı temsil etmektedir.



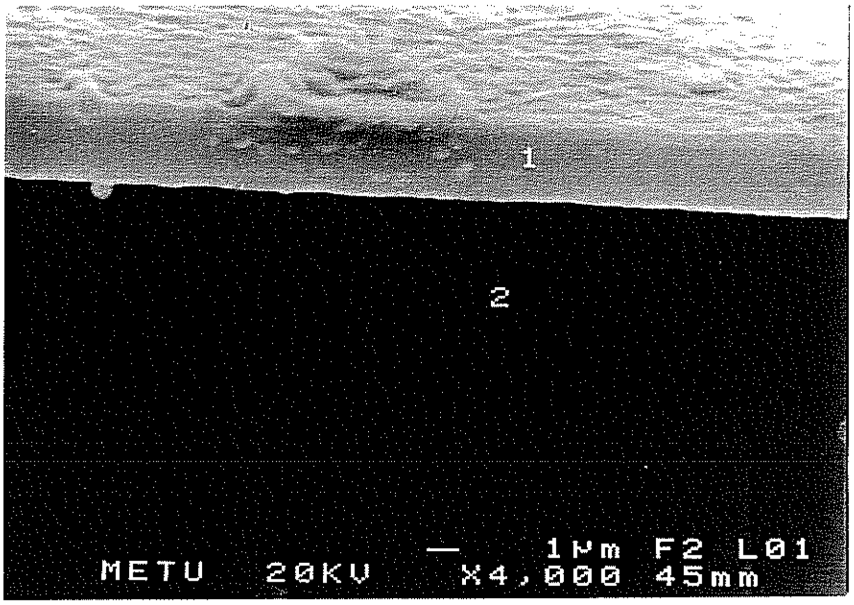
Şekil 4.13. Üre kullanılarak Si altlık üzerinde elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT film yüzeyinin SEM görüntüsü.



Şekil 4.14. Üre kullanılarak Pt kaplanmış Si üzerinde elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT filmin SEM görüntüsü.



Şekil 4.15. Üre kullanılmadan Pt kaplanmış Si altlık üzerinde elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT film yüzeyinin SEM görüntüsü.



Şekil 4.16. Üre kullanılarak Pt kaplanmış Si üzerinde elde edilen ve 850°C'de 5 saat süreyle ısıl işleme tabi tutulan PZT filmin SEM görüntüsü. Şekilde 1 numaralı bölge PZT filmi, 2 numaralı bölge ise Si altlığı temsil etmektedir.

4.6. Kimyasal Yolla Sentezlenen $PbZrO_3$'ün Karakterizasyonu

Proje raporunun bundan önceki bölümlerinde $Pb(Zr,Ti)O_3$ kompozisyonundaki filmlerin ve tozların üretimi ile bu konuda karşılaşılan güçlüklerin çözümü için geliştirilen yöntemler verilmişti. PZT kompozisyonundaki filmlerin elde edilmesinde başlangıçta kullanılan çözeltilerden çökeltme (precipitation) yöntemiyle aynı kompozisyondaki tozları da elde etmek mümkün olduğundan projede bu çalışmalara da yer verilmiştir. Ayrıca başlangıçta hazırlanan stok çözeltiler kullanılarak $PbZrO_3$ ve $PbTiO_3$ toz ve filmlerini de elde etmek mümkündür. Enerji depolaması için çok uygun bir malzeme olarak son zamanlarda sıklıkla çalışılan $PbZrO_3$ üzerine projede yapılan çalışmalar da aşağıda yer almaktadır.

Kurşun zirkonat ($PbZrO_3$) 230 °C Curie sıcaklığına sahip antiferroelektrik bir malzeme olarak bilinmektedir. Proje çalışmalarında $Pb(Zr,Ti)O_3$ filmler için hazırlanan stok solüsyonlarını kullanarak aynı anda $PbZrO_3$ elde etmekte mümkün olduğundan, bu maddenin de çalışılması yoluna gidilmiştir. Antiferroelektrik-ferroelektrik dönüşümü kuvvetli bir elektrik alan altında gerçekleştiğinden, $PbZrO_3$ enerji depolanması için çok uygun bir malzeme olarak kabul edilmektedir. Ayrıca mikrodalga dielektrik özellikleri de üzerinde yoğunlukla çalışılan bir konudur.

$Pb(Zr,Ti)O_3$ eldesinde olduğu gibi kurşun zirkonatta ikili oksit sisteminin karıştırılıp sinterlenmesi gibi konvansiyonel yöntemlerle üretildiği zaman 1200 °C'de en az 2 saat sinterleme gerektirmektedir ki, bu sıcaklıklarda PbO uçuculuğu çok fazladır. Bu nedenle çalışmamızda PZT tozları ve filmlerinde olduğu gibi, $PbZrO_3$ üretiminde de sol-gel yöntemi uygulanmıştır. Başlangıç malzemeleri olarak $PbCl_2$ ve $ZrCl_4$ ile üre stok solüsyonları kullanılmıştır. Üredeki ayrışım hızı çok düşük olduğundan, elde edilen tozların boyutları mikronaltı büyüklüklerden birkaç mikrona kadar değişmektedir. Buna karşılık üre kullanılmadan elde edilen aynı kompozisyondaki tozların büyüklükleri ise 10 - 50 μm arasında değişmektedir. Böylece üre kullanılarak yapılan homojen çökeltme işleminde mikron büyüklükte, homojen tozlar elde edilebildiği anlaşılmıştır.

Stok çözeltilerden $PbZrO_3$ kompozisyonunu elde edecek miktarlarda alınan nümuneler saf suda çözülmüşlerdir. Solüsyon 90 °C'deki etüvde 2 saat tutulmuştur. Bu işlem sonrasında çökelen partiküller filtre kağıdı ile süzüldükten sonra suyunu almak için 90°C'de bir gece bırakılmışlardır.

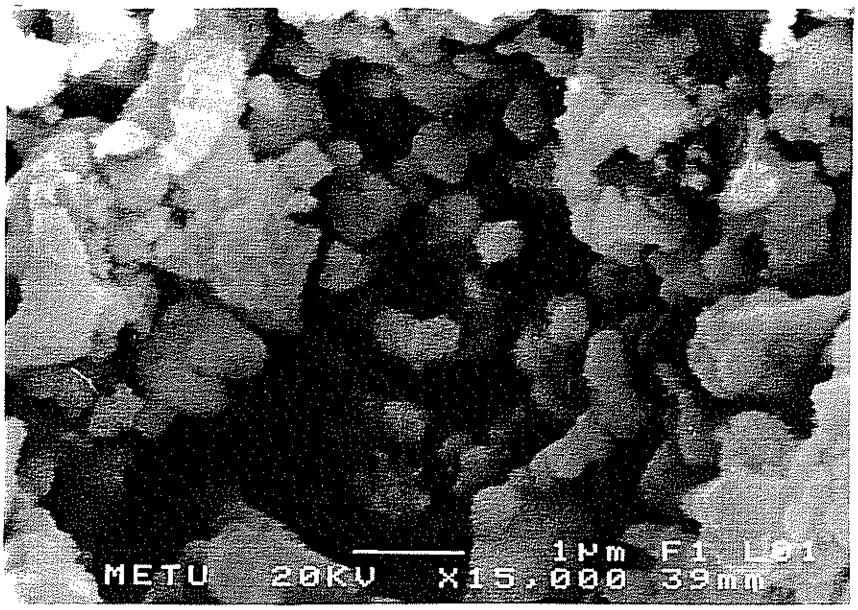
Elde edilen tozlar Tarama Elektron Mikroskobu (SEM) ile çalışmayı kolaylaştırmak amacıyla düşük basınçta preslendikten sonra 25 nm kalınlığında Au-Pd alaşımı ile kaplanmıştır. Üre kullanılarak elde edilen tozların görüntüleri Şekil 4.17'de verilmektedir. Bu tozların mikron boyutlarında olması, kullanılan yöntemin homojen ve mikron boyutlarında toz elde etmek için uygun bir yöntem olduğunu ortaya koymaktadır. Şekil 4.18'de verilen EDS analizi neticesinde ise 70% Pb, 30% Zr elde edilmiştir ki, bu da üretilen tozların istenen stokyometrik oranda olduğunu göstermektedir.

Üre kullanılmadan elde edilen tozların görüntüsü ise Şekil 4.19'da verilmektedir. Bu şekilde görülebileceği gibi tozların morfolojisi oldukça farklı olup büyük parçacıklar halinde oluşmakta ve EDS analizleri de 85% Pb, 15% Zr vermektedir. Bu durumda üre kullanılmadan elde edilen tozların kurşunca zengin bölgeler içerdiği ve istenen stokyometrik kompozisyonun kurşunca zengin bölümünde yer aldığı anlaşılmaktadır (Şekil 4.20).

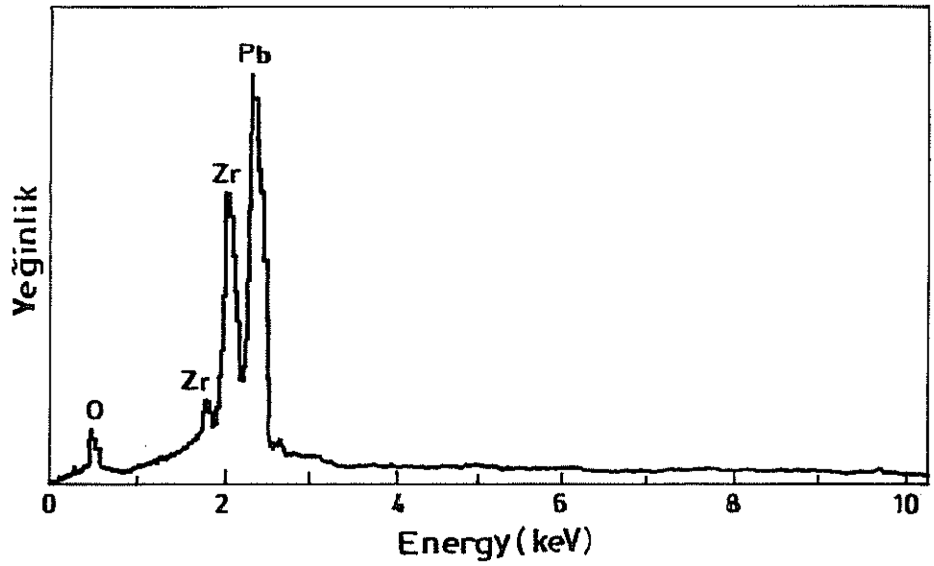
Daha sonra 350-850°C arasında havada 6 saatlik ısıl işleme tabi tutulan tozların XRD spektrumları Şekil 4.20'de verilmektedir. Bu spektrumların da gösterdiği gibi 850°C'lik ısıl işlemde ikincil fazlar görülmemekte ve bu sıcaklık homojen bir faz eldesi için yeterli olmaktadır. Oluşan faz tetragonal $PbZrO_3$ olup kafes parametreleri ve birim kafes hacmi aşağıdaki Tablo 7'de verilmektedir.

Tablo 7. 850°C'de 6 saat süre ile ısıl işleme tabi tutulan $PbZrO_3$ tozların kristal parametreleri.

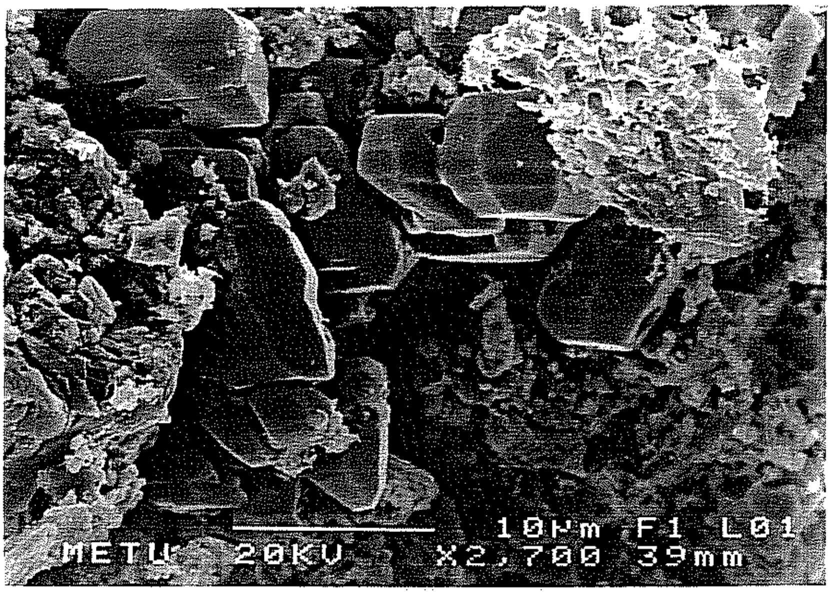
Kristal Yapı : Tetragonal	
a = 11.768958 Å	α = 90.0000°
b = 11.768958 Å	β = 90.0000°
c = 8.229188 Å	γ = 90.0000°
Birim Kafes Hacmi : 1139.81 Å^3	



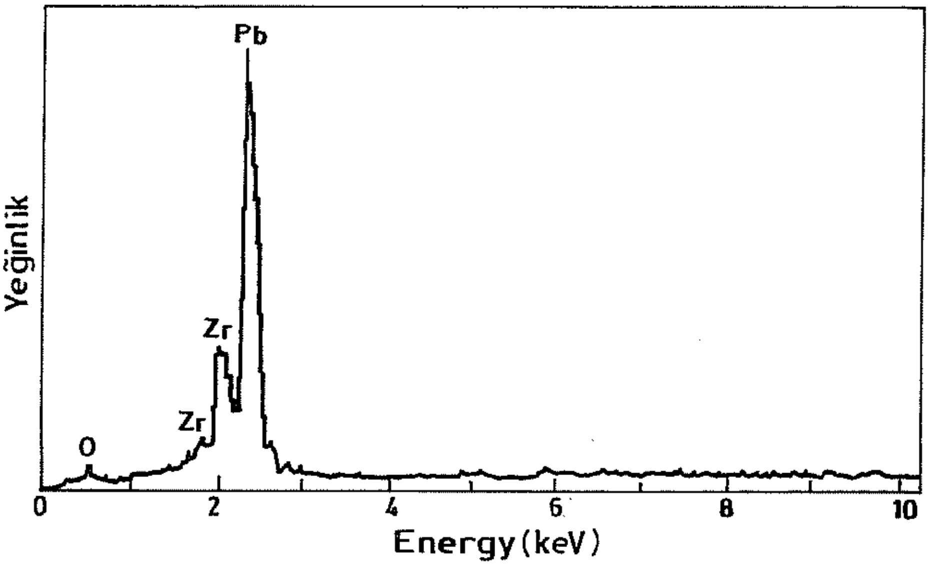
Şekil 4.17. Üre kullanılarak elde edilen $PbZrO_3$ tozların SEM görüntüsü.



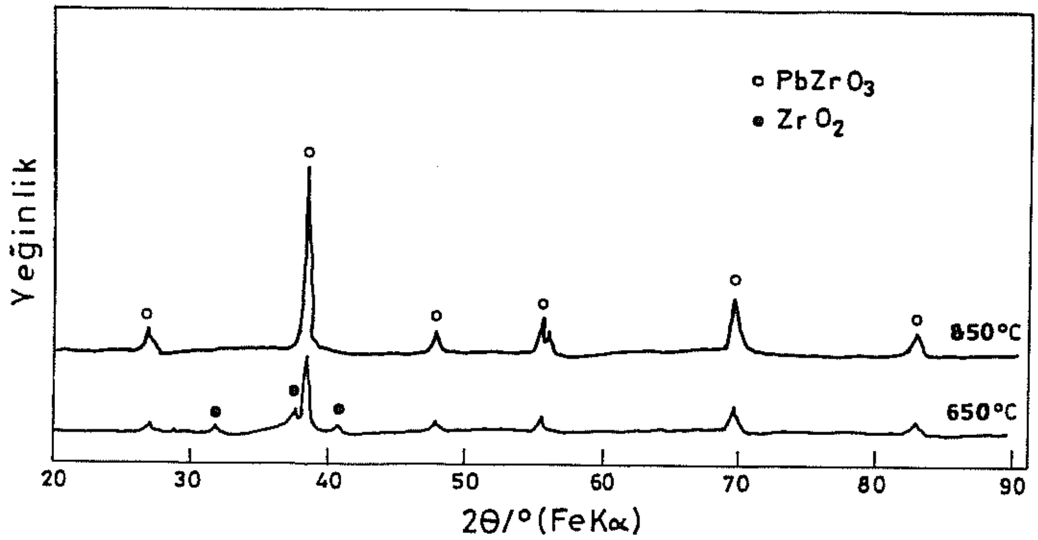
Şekil 4.18. Şekil 4.17'deki tozların EDS analizi.



Şekil 4.19. Üre kullanılmadan elde edilen $PbZrO_3$ tozların SEM görüntüsü.



Şekil 4.20. Şekil 4.19'da SEM görüntüsü verilen tozların EDS analizi.



Şekil 4.21. Üre kullanılarak elde edilen $PbZrO_3$ tozlarının ısıl işlem sonrası elde edilen XRD spektrumu.

4.7. Dielektrik Katsayısı Ölçümleri

PZT kompozisyonundaki filmlerin dielektrik katsayıları kapasitans ölçümleri yapılarak bulunmuştur. Kapasitans ölçümleri 1 MHz sabit frekans değerinde HP 4194A Empedans/Kazanç Fazı Analiz Cihazı kullanılarak gerçekleştirilmiştir. Kapasitans ölçümleri için platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmler kullanılmıştır. Üre kullanılmadan elde edilen filmlerin yüzeyleri oldukça pürüzlü olduğundan ölçümler sağlıklı sonuçlar vermemiştir. Bunun sebebinin bu filmlerdeki altlığa yapışmanın az olması nedeniyle oldukça gözenekli yapıda film eldesi olduğu düşünülmektedir.

PZT kompozisyonundaki filmlerin dielektrik katsayıları kapasitans ölçümlerinden faydalanarak ve aşağıdaki bağıntı kullanılarak hesaplanmıştır.

$$K = (C \times t) / (\varepsilon_0 \times A)$$

Bu bağıntıda

C = Nümunenin ölçülen kapasitans değeri, Farad

A = Nümunede ölçüm yapılan bölgenin alanı, m^2

ε_0 = Vakum dielektrik permitivitesi, 8.85×10^{-12} F/m
t = filmin kalınlığı, m

Platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmlerde yapılan çeşitli ölçümler sonucunda elde edilen dielektrik katsayısı 480-600 arasında değişmektedir. Bu değerlerin ortalaması olarak elde edilen dielektrik katsayısı değeri ise 562 olarak bulunmuştur.

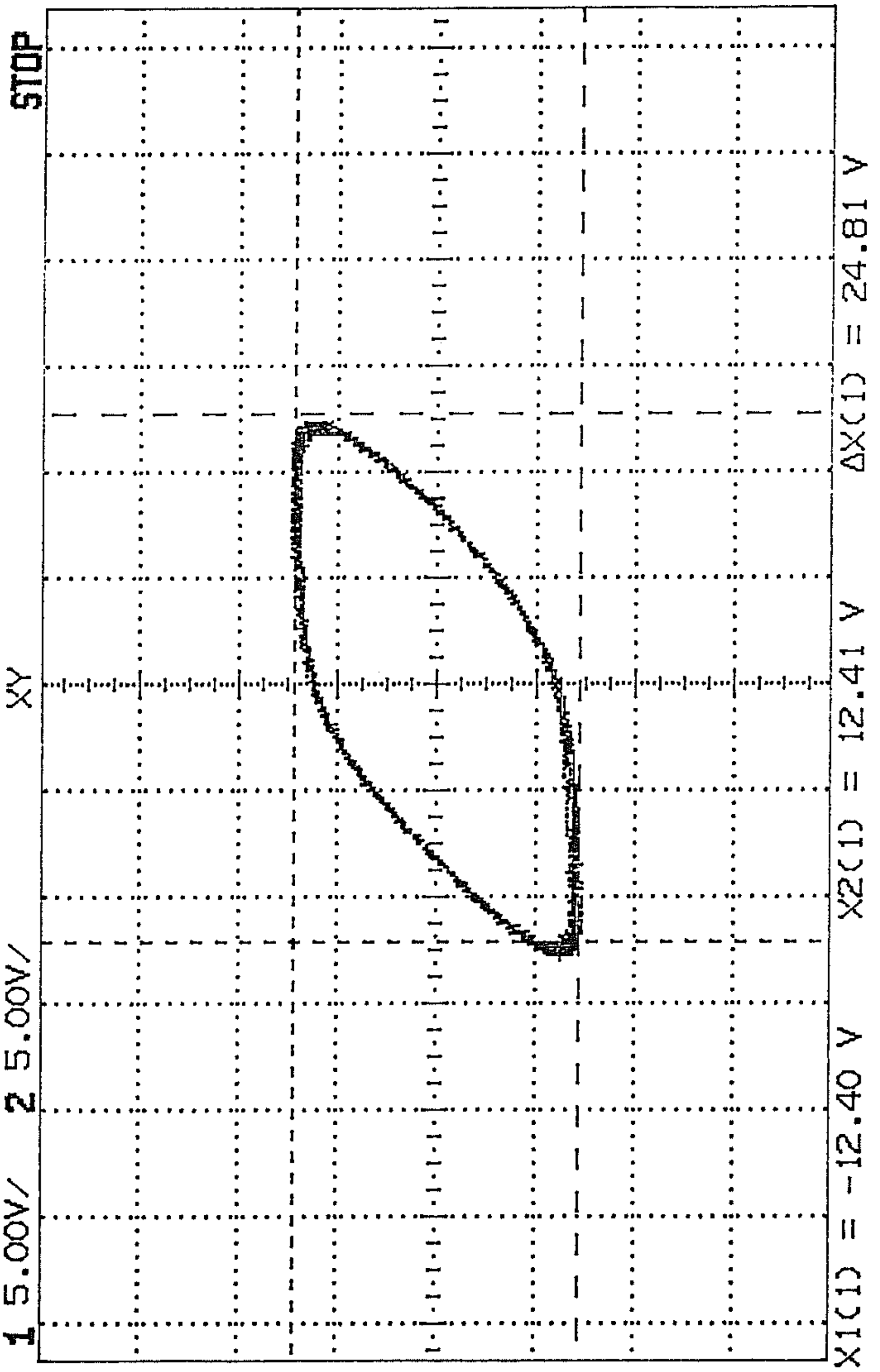
4.8. Ferroelektrik Histeresis Döngüsü Ölçümleri

PZT filmlerin ferroelektrik histeresis döngüsü ferroelektrik davranışı belirleyen parametreler olan artık polarizasyon (P_r) ve koersiv alan (E_c) değerlerini vermektedir. Bu histeresis döngüsünü tesbit etmek amacıyla standart Sawyer-Tower devresi kullanılarak polarizasyon histeresis döngüsü elde edilmiştir (Sawyer ve Tower, 1930). Bu ölçümlerde de yukarıdaki bölümde açıklanan nedenlerden dolayı platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmler kullanılmıştır. İletken uçlar yine gümüş kolloid boya yardımıyla hazırlanmıştır. Sawyer-Tower devresi kullanılarak sayısal bir osiloskop yardımıyla X ve Y eksenleri boyunca voltaj değişimleri kaydedilmiş ve polarizasyon histeresis döngüsü elde edilmiştir.

Ölçülen nümunelerde osiloskoptan elde edilen örnek bir görüntü Şekil 4.22'de verilmektedir. Bu histeresis döngüsünden elde edilen X ve Y eksenleri boyunca değişen voltaj değerleri ile aşağıdaki bağıntılar kullanılarak polarizasyon döngüsü elde edilmiştir.

X Ekseni : Elektrik Alan = (V_x / Film kalınlığı) (volt/m)
Y Ekseni : Polarizasyon = (Q / A) (kulomb/m^2)
Q (elektrik yük) = C x Vy (kulomb)
C = Kapasitans (Standart devrede 1 nF olarak kullanılmıştır)
A = Nümunede ölçüm yapılan bölgenin alanı, m^2

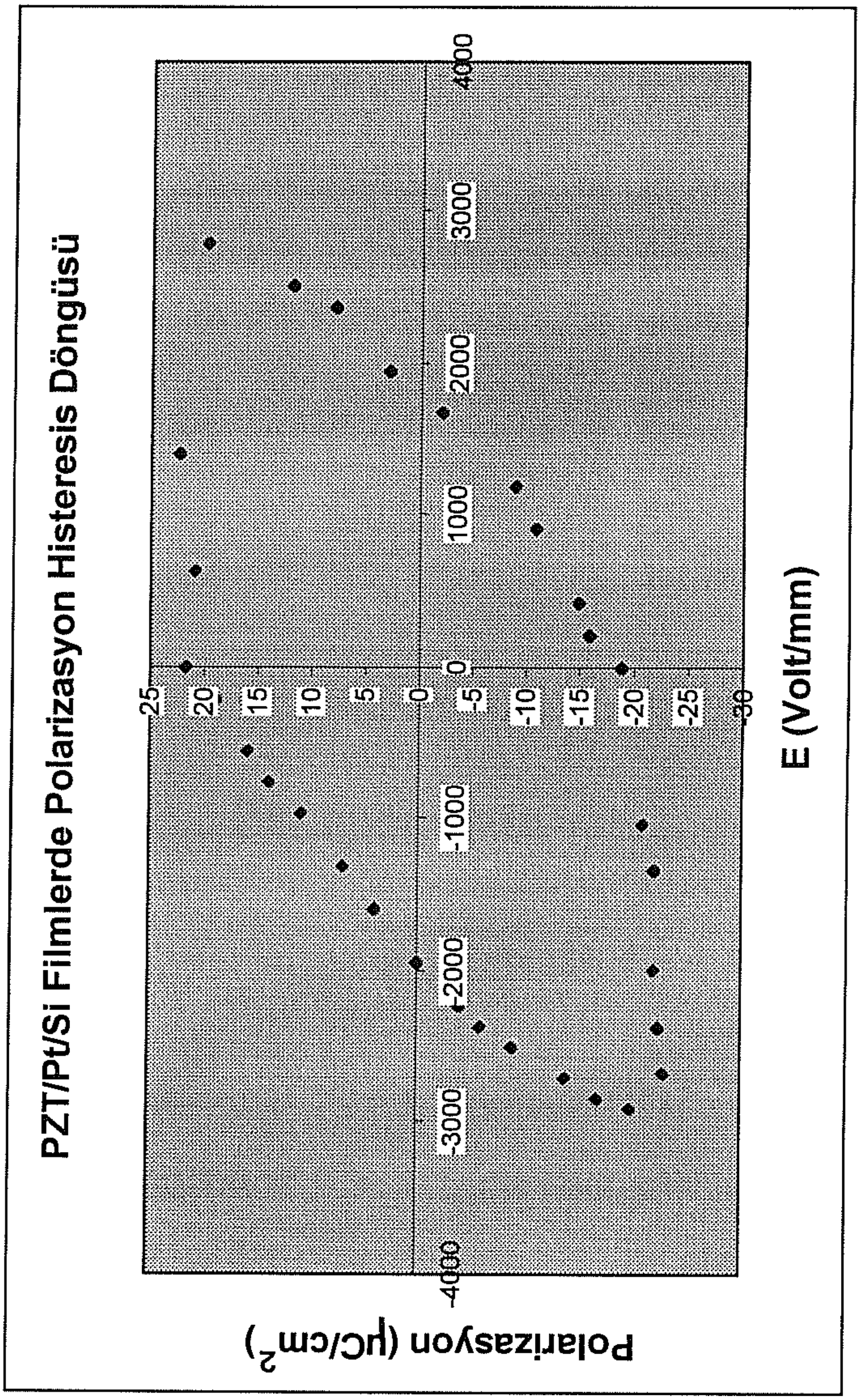
Şekil 4.22'de görülen V_x ve V_y değerleri kullanılarak elde edilen polarizasyon ve elektrik alan değerleri Tablo 8'de ve bu değerler yardımıyla bulunan polarizasyon histeresis döngüsü de Şekil 4.23'de verilmektedir. Şekil 4.23'den elde edilen artık polarizasyon (P_r) ve koersiv alan (E_c) değerleri, ~22 μC/cm^2 ve ~20 kV/cm, olarak belirlenmiştir. Bu değerler literatürde elde edilen çalışmalarla (Tablo 9) uyum göstermektedir. Ayrıca bizim çalışmamızda elde edilen değerler hacimsel PZT seramikler için bulunan değerlere de yakın değerler olarak göze çarpmaktadır.



Şekil 4.22. Standart Sawyer-Tower devresi kullanılarak PZT kompozisyonundaki filmlerden elde edilen sayısal osiloskop görüntüsü.

Tablo8. Polarizasyon histeresis döngüsü için kullanılan değerler.

X(volt)	Y(volt)	E (volt/mm)	Polarizasyon($\mu C/cm^2$)
0	6.81	0	21.68
0	-5.91	0	-18.81
2.81	6.56	624.44	20.89
6.25	7.03	1388.88	22.39
12.50	6.25	2777.77	19.90
0.93	-5.00	206.66	-15.92
1.88	-4.68	416.66	-14.90
4.06	-3.43	902.22	-10.92
5.31	-2.81	1180.00	-8.95
7.50	-0.63	1666.66	-1.99
8.75	0.93	1944.44	2.96
10.63	2.50	2361.11	7.96
11.25	3.75	2500.00	11.94
12.50	6.25	2777.77	19.90
-8.75	0	-1944.44	0
-7.18	1.25	-1595.55	3.98
-5.93	2.18	-1317.77	6.94
-4.37	3.43	-971.11	10.92
-3.43	4.37	-762.22	13.92
-2.50	5.00	-555.55	15.92
-0.93	5.93	-206.66	18.89
-9.06	-0.93	-2013.33	-2.96
-10.00	-1.25	-2222.22	-3.98
-10.63	-1.88	-2361.11	-5.97
-11.25	-2.81	-2500.00	-8.95
-12.18	-4.37	-2706.66	-13.92
-12.81	-5.31	-2846.66	-16.91
-13.12	-6.25	-2915.55	-19.90
0	-5.93	0	-18.89
-1.25	-6.25	-277.77	-19.90
-4.68	-6.56	-1040.00	-20.89
-6.05	-6.91	-1345.00	-0.22
-11.25	-6.88	-2370.00	-0.22
-12.04	-7.20	-2675.55	-0.23
-8.94	-6.91	-1987.00	-0.22



Şekil 4.23. Platin kaplı Si altlıklar üzerinde elde edilen PZT filmlerin polarizasyon histeresis döngüsü.

Tablo 9. PZT filmler için literatürden elde edilen bazı ferroelektrik parametreler.

No	Üretim Metodu	Altlık	E_c	P_r(μC/cm^2)	Dielektrik Katsayısı	Kaynak
1	Sol-jel	Pt/Ti/SiO$_2$/Si	3.3 V PZT(20/80) 2.5 V PZT(30/70) 2.4 V PZT(40/60) 2.1 V PZT(53/47)	42.6 PZT(20/80) 36.7 PZT(30/70) 34.1 PZT(40/60) 30.3 PZT(53/47)	-	Zhu, et.al., 1998
2	RF Püskürtme	Pt(111)/Ti/SiO$_2$/Si	100 kV /cm (1 kHz) 120 kV /cm (10 kHz) 225 kV /cm (10 kHz)	-	-	Du ve Chen, 1998
3	Sol-jel	İndium-Sn oksit/7059	81.6 kV /cm	21.8	340	Yi, et. al., 1990
4	Sol-jel	Pt/(100) Si	85 kV /cm	20	-	Chu, et. al., 1998
5	Sol-jel	Pt/Si	-	20	1100	Teowee, et. al., 1998
6	Sol-jel	(100) Si	5*10^6 V/m	20	350	Li, et. al., 1994
7	Sol-jel	Pt/Si	20 kV /cm	35	350-400	Barrow, et. al., 1997
8	Sol-jel	Pt/Al	9-24 V/μm	28-50	-	Sporn, et. al., 1995
9	Sol-jel	Pt/Ti/SiO$_2$/Si	3 V	32	800-1000	Zavala ve Fendler, 1997
10	Sol-jel	Pt/Ti/SiO$_2$/Si	3 V	18	-	Troiler, et. al., 1996
11	Sol-jel	Al$_2$O$_3$	26.7 kV /cm	6.6	260	Yi, et. al., 1988

Malzeme	E_c (kV /cm)	P_r (μC/cm^2)	Dielektrik Katsayısı
Kütlesel PZT	≈50	≈30	≈1000
Bu çalışmada Pt/Si üzerine üre kullanılarak kaplanan PZT filmler	~20	~22	~562

SONUÇLAR

Bu çalışmada ferroelektrik özellikli $Pb(Zr,Ti)O_3$ filmler ve tozlar sol-jel yöntemi vasıtasıyla metal klorürler kullanılarak elde edilmiştir. Tozlar sulu çözeltiden homojen çökeltme, filmler ise çökelme öncesi daldırma yöntemi kullanılarak üreli ortamda hazırlanmışlardır. Altlık malzemesi olarak platin kaplanmış Si-(111) dilimleri, Si dilimleri ve α-Al_2O_3 kullanılmıştır. Bu yöntemle elde edilen filmlere literatürde ilk kez rastlanmaktadır.

Filmlerin ve tozların karakterizasyon işlemleri için öncelikle XRD ve SEM/EDS kullanılmıştır. Parça boyutu, morfolojisi ve film yüzeyleri SEM çalışmaları ile gözlemlenmiş, film ve toz bileşimleri EDS analizleri alınarak araştırılmıştır. Isıl işlem esnasında bir kaç kez XRD analizleri alınarak oluşan fazlar belirlenmiştir. Toz örneklerin içerdiği safsızlıkların belirlenebilmesi amacı ile spektroskopik IR analizleri yapılmıştır.

850°C'de, 5 saat boyunca ısıl işleme tabi tutulmuş bütün tozlar ve filmlerin perovskit faza geçerek tamamen kristalize olduğu ve stokyometrik olduğu belirlenmiştir. 350°-650°C ısıl işlem sıcaklıkları arasında perovskit, piroklor, ve kurşun titanyum, 650-850°C arasında ise perovskit ve piroklor fazlar gözlemlenmiştir. Hazırlanan PZT tozların küçük, düzgün ve homojen dağılımlı parça yapısında olduğu, ancak filmlerin bileşimlerinin yer yer homojen olmadığı belirlenmiştir. Platin kaplanmış silisyum ve alumina altlıklar üzerindeki ıslanmanın, platin kaplanmamış silisyum üzerindekine göre daha fazla olduğu gözlemlenmiştir. Ayrıca üre kullanılarak elde edilen çözeltilerden üretilen filmlerde yüzey daha düzgün ve altlığa yapışma daha fazla olarak belirlenmiştir.

Platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmlerin polarizasyon histeresis eğrisinden elde edilen artık polarizasyon (P_r) ve koersiv alan (E_c) değerleri, ~22 $\mu C/cm^2$ ve ~20 kV/cm, olarak belirlenmiştir. Aynı filmlerde dielektrik katsayısı ise 562 olarak hesaplanmıştır.

ÖNERİLER

- Elektronik ve optik endüstrisindeki önemi açısından ferroelektrik seramik oksit ince film çalışmalarına devam edilmelidir.

- Özellikle film çalışmalarında kullanılan ısıl işlem sürelerinin uzun olması arayüzey tepkimelerinin artmasına neden olduğundan, hızlı ısıl işlem (rapid thermal annealing) gibi yöntemler denenmelidir.

- Kararlı yapıdaki ferroelektrik filmlerin tekrar edilebilir bir biçimde üretilmesi amacıyla çeşitli altlıklar üzerindeki çekirdeklenme ve büyüme mekanizmaları da çalışılmalıdır.

- Çeşitli ferroelektrik ve piezoelektrik parametrelerin ölçümü için kullanılan cihazlar daha çok kütlesel nümunelere uygun olduğundan, film özelliklerinin ölçümü için uygun cihazların geliştirilmesi gereklidir.

- Bu malzemelerdeki özellik-yapı ilişkilerini güvenilir biçimde ortaya çıkarmak için nano boyutlarda çalışmak gereklidir. Bu nedenle böyle malzemeler hazırlanabilmesi için mikrokalıplama benzeri yöntemlerden yararlanılmalı ve ölçümler için de atomik kuvvet mikroskobu gibi teknikler kullanılmalıdır.

PROJE KAPSAMINDA YÜRÜTÜLEN TEZ ÇALIŞMALARI

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  (Tezin abstract bölümü ekte verilmektedir).
- Micropatterning of Ferroelectric Thin Films and Size Effects, N Turhan, M.S. Tezi, ODTÜ, devam ediyor.

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- M. Özenbaş and Ergin, S. Ü., "Preparation of Ferroelectric Thin Films by Homogeneous Precipitation and Their Characterization", 8th European Meeting on Ferroelectricity, 4-8 Temmuz 1995, Nijmegen, Holland, P12-26.
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- M. Özenbaş, "Sol-Gel Processing and Characterization of Ferroelectric $Pb(Zr,Ti)O_3$ Films and Powders", MRS Fall Meeting, 1-5 December 1997, Boston, USA, p.495.

Bu yayınlar ekte verilmektedir.

AVRUPA COST-514 PROJESİ

COST 514 projesi Avrupa Topluluğuna bağlı üye ülkelerin katılımıyla oluşan uluslararası nitelikte bir projedir. Projeye katılım senede iki kez düzenlenen MC (Management Committee) toplantılarında diğer üyelerin onaylaması koşuluyla kabul edilmektedir.

Proje önerimiz 1994 yılının ikinci MC toplantısında (4 Eylül 1994 - Aachen - Almanya) gündeme gelmiş ve tartışılarak kabul edilmiştir. Projede işbirliği yapan enstitü veya laboratuvarların bir listesi (COST-514 Projesi Üyeleri) ekte verilmektedir. Ayrıca her ülkeden onaylanan bir temsilci de Yürütme Kurulunun (MC- Management Committee) üyesi olmaktadır. Bu kurulunda bir listesi ekte sunulmaktadır.

COST 514 projesi bizim de içinde bulunduğumuz grup benzeri küçük çalışma gruplarından oluşmakta ve her bir grubun çalışma raporu daha sonra bir araya getirilerek tartışılmaktadır.

COST 514 projesinde ferroelektrik filmleri üretmek için kullandığımız yöntem yaptığımız literatür çalışması neticesinde tesbit edilmiş ve partner laboratuvarlara da üretim yöntemimiz hakkında bilgi verilmiştir.

1995 yılının ilk MC toplantısı ile birlikte bir Çalışma Toplantısı da düzenlenmiş ve 16-17 Şubat 1995 tarihlerinde COST 514 projesi içerisinde çalışan tüm grupların ve bazı davetli konuşmacıların katıldığı bu toplantı İsviçre Lozan'da EPFL'de gerçekleştirilmiştir. Bizim çalışmamız henüz başlangıç safhasında olmasına rağmen programda yer almıştır. Program ve sunduğumuz tebliğ ekte verilmektedir.

1995 yılının ikinci MC toplantısı ise 5 Temmuz 1995 tarihinde Hollanda'nın Nijmegen kentinde yapılmıştır. Bu toplantıda ele alınan 1994 yılı çalışmaları topluca incelenmiş ve sonuçlar bir rapor halinde sunulmuştur. Bu raporun bir kopyası ekte verilmektedir.

Hollanda'da düzenlenen MC toplantısı 8th European Meeting on Ferroelectricity (4-8 Temmuz 1995, Nijmegen) Kongresi sırasında yapılmıştır. Bu kongreye de çalışmalarımızın sonuçları bir tebliğ halinde sunulmuştur. Tebliğ "Preparation of $Pb(Zr,Ti)O_3$ Thin Films and Powders by the Sol-Gel Process" Ferroelectrics dergisinde de yayınlanmıştır.

1996 yılının ilk Yürütme Komitesi (MC-Management Committee) toplantısı 3 Mart 1996 tarihinde Madrid - İspanya'da yapılmıştır. Madrid'de düzenlenen MC toplantısı "Ferroelectric

Thin Films" Çalışma Toplantısı ile birlikte 4-5 Mart 1996 tarihlerinde COST 514 projesi içerisinde çalışan tüm grupların ve bazı davetli konuşmacıların katılımıyla Madrid'de Malzeme Araştırma Merkezinde gerçekleştirilmiştir. Bu toplantıda da çalışmalarımızın sonuçları bir tebliğ halinde sunulmuştur. Bu toplantının programı ile sunulan tebliğin "Preparation of PZT Films and Powders by the Sol-Gel Process" bir kopyası ekte sunulmaktadır.

COST-514 projesi kapsamında yaptığımız çalışmalar her sene COST tarafından düzenlenen Workshop tipi toplantılarda sunulmakta, ayrıca çalışmalara ait verilen raporlar da her iki senede bir hazırlanan bir COST kitapçığında yayınlanmaktadır. 1996 yılı çalışmalarına ait COST raporu da ekte verilmektedir. 1998 yılı başından itibaren projemiz TÜBİTAK açısından sonuç dönemine girdiğinden bu dönemden sonraki çalışmalara ancak şahsi düzeyde katılmak mümkün olabilecektir.

Avrupa COST projeleriyle ilgili en önemli husus Türkiye Avrupa Birliğinin bir üyesi olmadığından çalışmalarda yeteri kadar yer alamamaktadır. Tüm üye ülkeler toplantı masraflarını Avrupa Birliğinden sağladıklarından düzenli olarak toplantılara katılabilmekte ve sonuçlarını birbirleri ile sık aralıklarla tartışabilmektedirler. Türk katılımcılar ise ancak TÜBİTAK bütçesinden faydalanarak kısıtlı sayıdaki toplantılara katılabilme olanağı bulmaktadırlar. Ayrıca Avrupa Birliği üyesi ülkelerin araştırmacıları EU tarafından sağlanan desteklerle çeşitli sürelerde partner laboratuvarları ziyaret ederek çalışma imkanı bulmakta ve tecrübelerini arttırmaktadırlar. Fakat bu imkanlardan Türk araştırmacılar faydalanamamaktadır. Bu problem çözüldüğü takdirde COST projelerinden daha fazla yarar sağlanacağı açıktır.

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EKLER

EK A

PROJE KAPSAMINDA YÜRÜTÜLEN TEZ ÇALIŞMALARI

ABSTRACT

PREPARATION AND CHARACTERIZATION OF FERROELECTRIC $Pb(Zr,Ti)O_3$ FILMS

Ergin, S. Ümit
M.S., Department of Metallurgical and Materials Engineering
Supervisor: Prof. Dr. Macit Özenbaş
Co-Supervisor: Prof. Dr. Tarık Ö. Oğurtanı

January 1997, 81 pages

In this study, ferroelectric $Pb(Zr,Ti)O_3$ films and powders were prepared from metal chlorides using sol-gel processing method. For powders; homogeneous precipitation from aqueous solution and for films; dip coating just before precipitation was applied in the presence of urea, $[(NH_2)_2CO]$. Pt-coated Si (111) wafers, Si wafers and α-Al_2O_3 were employed as substrates all through this study.

Sol-gel processing method was used throughout the study, because it is a reliable, compositionally adjustable and inexpensive method for the production of ferroelectric films.

Characterization of the films and powders were carried out primarily by XRD and SEM/EDX. The particle size and morphology, and film surfaces were observed during SEM studies, while compositions of the films and powders were investigated by EDX analyses. Phases formed upon annealing were determined by

XRD of the samples at several stages of annealing. In order to accurately determine the impurities remained in the powder samples, IR spectroscopic analyses were carried out.

Both the films and powders were stoichiometric and completely crystallized into perovskite phase after annealing for 5 hours at 850^{0}C. For annealing temperatures between 350 and 650^{0}C, perovskite, pyrochlore, lead titanate, and for those between 650 and 850°C, pyrochlore and perovskite phases were observed. The PZT powders had homogeneously distributed, fine particle sizes and morphology; however, the films prepared were partly deviated from compositional homogeneity. The films have better wetting characteristics on alumina and Pt-coated Si substrates than that on bare silicon substrates.

Keywords: PZT, Ferroelectric films, Sol-gel processing

EK B

PROJE KAPSAMINDA GERÇEKLEŞTİRİLEN YAYINLAR

COST 514

Ferroelectric Thin Films Workshop

EPFL CO 22, Thursday, February 16, 1995

08.00-08.20 **Registration**
08.20-08.30 **Introductory Remarks - N. Setter**

08.30-09.00 KEYNOTE TALK

Progress and Opportunities in Ferroelectric Memories and Sensors
W. Wersing, Siemens, Munich, Germany

09.00-10.20 ELECTRICAL PROPERTIES

09.00-09.20 **Evaluation of DC Leakage Currents**
Geert Willems, IMEC Division MAP-ARS,
Kapeldreef 75 B-3001 Leuven, Belgium

09.20-09.40 **Study of Fatigue Effect in PZT Thin Films**
Enrico Colla, Laboratoire de Céramique, Ecole Polytechnique Fédérale de Lausanne, MX-C (Ecublens) CH1015 Lausanne, Lausanne, Switzerland

09.40-10.00 **The Role of Electrode and Substrate on PZT Properties**
Dirk Wouters, IMEC Division MAP-ARS,
Kapeldreef 75 B-3001 Leuven, Belgium

10.00-10.20 **Recent Results on Relaxation, Conduction, and Breakdown of Perovskite-Type Dielectric Thin Films**
Guido W. Dietz, Susanne Hoffman, Institut Für Werkstoffe der Elektrotechnik II RWTH Aachen, Sommerfeldstr. 24
52074 Aachen, Germany

[10.20-10.40 - COFFEE]

[10.15-10.30 - COFFEE]

10.30-12.00 GROUP DISCUSSIONS

[12.00-14.00 LUNCH]

14.00-15.00 GROUP DISCUSSIONS

15.00-16.00 GROUP COORDINATORS PRESENTATIONS

15.00-15.15 Group 1 - S. Leppävouri

15.15-15.30 Group 2 - L. Pardo

15.30-15.45 Group 3 - D. Wouters

15.45-16.00 Group 4 - M. Kosec

16.00-16.40 GENERAL DISCUSSIONS

(Laboratory visits of LC are possible during this time)

16.40 Closing

Additional Information:

Hotel: Movenpick Radisson, Ouchy - see enclosed map. When checking in, please indicate that you are with the group visiting EPFL. Reservatations have been made in advance.

Registration Fee: No Registration Fee

Meals: The cost for the meals will be 120 SFr per person, to include lunch on Thursday and Friday, dinner on Thursday and coffee breaks. To be paid during registration on Thursday morning.

*** Annual Report ***

A COST 514 annual report will be generated from the presentations given at the meeting. Each project coordinator is asked to submit a 3-4 page report or presentation summary at the beginnning of the meeting.

10.40-12.00 LASER ABLATION DEPOSITION

10.40-11.00 **Laser Ablation Deposition of PZT Thin Films and Heterostructures**
Seppo Leppävuori, J. Levoska/ J. Lappalainen, University of Oulu, Dept. of Electrical Engineering, Microelectronics Laboratory, FIN-90570, Oulu, Finland

11.00-11.20 **PST/YBCO Heterostructures by Laser Ablation**
Carl A. Björmander, Dept. of Condensed Matter Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

11.20-11.40 **Laser Deposition of PZT Thin Films and In-Situ Diagnostics of the Process**
Francesco Fuso, Dipartimento de Fisica, Univ. di Pisa, Piazza Toricelli 2, I-56100 Pisa, Italy

11.40-12.00 **Properties of Very Thin Ferroelectric Thin Films and Heterostructures Deposited by Laser Ablation**
K. Sreenivas, Dept. of Condensed Matter Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

[12.00-14.00 LUNCH]

14.00-15.20 CHARACTERIZATION

14.00-14.20 **TEM of Ferroelectric Thin Films**
Ian M. Reaney, University of Sheffield, Department of Engineering Materials, Sheffield, S1 4DU, England

14.20-14.40 **Advances in Preparation and Characterization of Ca Modified PT Thin Films**
J. Mendiola, M.L. Calzada, L. Pardo, Dpto. de Materiales Ferroeléctr., ICMM-A., CSIC Serrano 144, E-28006 Madrid, Spain

14.40-15.00 **Investigation of PZT Formation by High Temperature X-ray diffraction**
Oleg Babushkin, Ture Lindbäck, Luleå University of Technology, Division of Engineering Materials, S-951 87 Luleå, Sweden

15.00-15.20 **Preparation and Characterization of $LiTaO_3$ Thin Films**
Charles-Henri Kohli, Philippe Schmid, Francis Lévy, Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH 1015 Lausanne, Switzerland

15.20-16.20 SOL-GEL PROCESSING

15.20-15.40 **Analytical Electron Microscopy Study of Sol-Gel Derived PLZT Thin Films and Powders**
Goran Drajic, Marija Kosec, Barbara Malic, Uras Delalut, "Josef Stefan" Institute, University of Ljubliana, Jamova 39, 61111 Ljubljana, Slovenia

15.40-16.00 **An Optimized Modified Sol-Gel Process for Making P(L)ZT and PMN(T) based Thin Films on Microelectronic Structures**
J. Hector, P. Gaucher, Thomson CSF, Lab. de Recherches, Domain de Corbeville, 91404 Orsay Cedex, France

16.00-16.20 **Preparation and Characterization of Ferroelectric Thin Films by Sol-Gel Processing Using Urea**
Macit Ozenbas, Middle East Technical University, Dept. of Metallurgical Engineering, 06531 Ankara, Turkey

[16.20-16.40 - Coffee]

16.40-18.30 MANAGEMENT COMMITTEE MEETING

[19.30 - DINNER AT RESTAURANT DE LA NAVIGATION, OUCHY]

* * *

Friday, February 17,1995

08.30-10.00 SPECIAL SESSION

08.30-09.15 *INVITED TALK*
Defect Chemistry of PZT Thin Films
D.M. Smyth *Lehigh University, Whitaker Laboratory 5, Bethlehem Pennsylvania 18015, United States*

09.15-09.45 **Progress in Ferroelectric Capacitor Stacks for Non-Volatile Memories**
Bernard Watts, Instituto MASPEC/CNR, Via Chiavari 18a, I-43100 Parma, Italy

09.45-10.15 **Modeling of Thin Film Pyroelectric Materials and Devices**
Andrew Bell, Laboratoire de Ceramique, Ecole Polytechnique Fédérale de Lausanne, MX-C (Ecublens) CH 1015 Lausanne

PREPARATION AND CHARACTERIZATION OF FERROELECTRIC THIN FILMS BY SOL-GEL PROCESSING USING UREA

Macit ÖZENBAŞ
Dept. of Metallurgical Engineering
Middle East Technical University
06531 - Ankara / TURKEY

Objective

Ferroelectric Ceramic Thin Films are non-metallic solid thin films that possess spontaneous polarization which can be reversed by an external electric field. Due to these unique properties, ferroelectric materials are used in various applications such as capacitors, piezoelectric materials (transducers), pyroelectric detectors, electro-optic materials, thermistors and dielectrics. The objective of the project is to promote a research for the preparation of ferroelectric thin films using homogeneous precipitation from aqueous solutions in the presence of urea [$(NH_2)_2CO$]. The details of the technique are given in the background section. The coating of the films was accomplished by dipping the substrates into the suspension of the powders. The films produced were characterized by using XRD and SEM for their structures and by piezometer and resistivity techniques for their properties. The investigation of the films and film/substrate interfaces by SEM and TEM can provide useful data for the interpretation of ferroelectric properties. Also, the microstructural data can supply some information about the reliability of the films. Another point of the electron microscopy work is the possibility of the investigation of growth mechanisms for these films.

Background

Preparation and synthesis conditions of uniform (preferably, monosized and monodispersed) and chemically homogeneous particles of ferroelectric ceramics (PZT, PLZT, $BaTiO_3$, $PbTiO_3$, $Sr_2Nb_2O_7$, $Ca_2Nb_2O_7$, $Sr_{0.5}Ba_{0.5}Nb_2O_6$, etc.) have been investigated, in the recent years, by numerous researchers [1-3] by using sol-gel/alkoxides, hydrothermal synthesis, and co-precipitation techniques.

The widely used precursors (in sol-gel techniques) for the preparation of PZT thin films include metal alkoxides such as lead acetate trihydrate, titanium isopropoxide and zirconium isopropoxide or zirconium isobutoxide. Since these alkoxides are extremely sensitive to moisture present in the ambient, their processing require a strictly controlled atmosphere which could be obtained by using a glove box. Multiple distillations (regular and vacuum) would also be necessary to remove the esters formed from the lead and PZT precursor solutions.

Preparation of PZT ceramic powders from the organic sols of citrates by the Pechini [4] method has recently been studied [5]. Because of the formation of a polyester resin during the synthesis that needs further heating (up to 800°C) to burn off the organic residue, XRD should not be the only available tool to check on the phase purity of the calcined product. Analytical tools like fourier-transformed IR spectroscopy and TGA should be accessible to verify the proper removal of carbonaceous residues when working with the Pechini method.

The oxalate method exemplified in the synthesis of lead barium titanate powders [6] is shown to produce high-purity, fine-grained but agglomerated, single-phase titanates by reacting barium- and lead-titanates with ammonium titanyl oxalate at low pH and low cation concentrations. It should be noted that the precursors and intermediates formed (oxalates) in this technique still requires a very strict control (such as IR spectroscopy) over the conversion-to-oxide step.

The coprecipitation method basically involves the titration of aqueous solutions of Pb, Ba, etc. salts (nitrates) and $TiCl_4$ in stoichiometric (or desired) quantities, in the presence of a hydrogen peroxide solution, against ammonia at a low temperature (such as 65°C) [7]. On the other hand, the precursors prepared with the nitrate-EDTA route produced fine but quite agglomerated particles of PZT composition [8]. In this route, $ZrCl_4$, and $Pb(NO_3)_2$ salt solutions were added gradually to the EDTA solution at a pH of 5, followed by 1 h of equilibriation at room temperature. The formed gel was then heated in a vacuum oven at 80°C for about 24 hours to produce the precursors.

The above were about all the methods tested previously in the synthesis of ferroelectric ceramic powders. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely the homogeneous precipitation from aqueous solutions. This method involves reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea [$(NH_2)_2CO$] in an aqueous solution in the temperature range 75-98°C to produce the precursors in about one hour. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia. Akınç, et al. [9] prepared spherical, monosized yttrium oxide precursor particles using urea and yttrium salt (nitrate or chloride) and $Y_3Al_5O_{12}$ using urea, yttrium- and aluminium nitrates. They were also successful in preparing uniform and chemically homogenous powders of $GdAlO_3$, $LaAlO_3$, and $GdAl_{11}O_8$. Therefore, this technique works in some systems quite well when one has the appropriate salts of the cation of the desired composition.

Preparation of Pb(Zr,Ti)O_3 Films

The required materials for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$ and $PbCl_2$, together with some urea. The stock solutions of lead, zirconium and titanium were prepared using the chlorides of these constituents. The concentrations studied are given below

Pb^{+2}	0.01 - 0.075 M
Zr^{+4}	0.1 - 0.5 M
Urea	0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, and urea to sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solution. The resulting PZT solutions were gelled by holding at 90°C for 1 to 2 hours while magnetically stirring. The starting pH of the solutions was between 0 and 1. However, the pH gradually increased to 5 - 5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution at these pH values. The precipitate was redissolved by adjusting the solution pH to yield gels of Pb(Zr,Ti)O_3.

XRD patterns were obtained for the dried precipitates, and also for the powders heat treated at 300 - 800°C in open alumina crucibles in air. Particle size and morphology were observed from SEM micrographs, which showed that the particles are of sub-micron size. EDX analysis were carried out on the same samples to have information about elemental distribution.

The substrate materials for PZT slurries (prepared from the produced powders) are platinized silicon and sapphire. The coating of the films was accomplished by dipping the substrates into the suspension of the powders. The next step in producing the films will be the use of a technique similar to spin-casting (e.g., with a centrifuge working minimally at about 3000 rpm; we are now working to build up such a centrifuge; by placing the substrate within a centrifuge tube or container together with the suspension of the powders).

The microstructure and characterization studies on these films are continuing.

References

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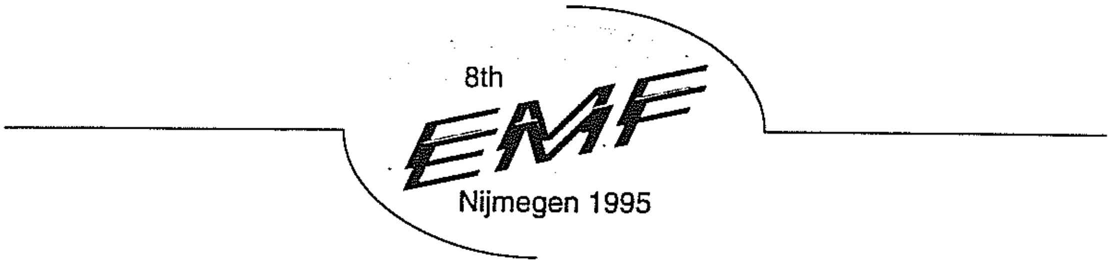

July 4-8, 1995
Nijmegen, The Netherlands

ABSTRACT BOOK

PREPARATION OF FERROELECTRIC THIN FILMS BY HOMOGENEOUS PRECIPITATION AND THEIR CHARACTERIZATION

Macit Ozenbas, and Umit Ergin

Dept. of Metallurgical Engineering
Middle East Technical University
06531 , Ankara , Turkey

Preparation and synthesis conditions of uniform and chemically homogeneous particles of ferroelectric ceramics (PZT, PLZT, $BaTiO_3$, $PbTiO_3$, $Sr_2Nb_2O_7$, $Ca_2Nb_2O_7$, $Sr0.5Ba0.5Nb_2O_6$, etc.) have been investigated, in the recent years, by numerous researchers by using sol-gel/alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely the homogeneous precipitation from aqueous solutions. This method involves reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea [$(NH_2)_2CO$] in an aqueous solution in the temperature range 75-98 C to produce the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia. The required materials for homogeneous precipitation are basically $ZrCl_4$; $TiCl_4$ and $PbCl_2$, together with some urea. The stock solutions of lead, zirconium and titanium were prepared using the chlorides of these constituents. The concentrations studied are given below:

Pb+2	0.001 - 0.005 M
Zr+4, Ti+4, Urea	0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, and urea to sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. The resulting PZT solutions were gelled by holding at 90 C for 1 to 2 hours while magnetically stirring. The starting pH of the solutions was between 0 and 1. However, the pH gradually increased to 5 - 5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution at these pH values. The precipitate was redissolved by adjusting the solution pH to yield gels of $Pb(Zr,Ti)O_3$. The substrate materials for PZT slurries (prepared from the produced powders) are platinized silicon and sapphire. The coating of the films was accomplished by dipping the substrates into the suspension of the powders. XRD patterns were obtained for the dried precipitates, and also for the powders and films heat treated at 300 - 800 C in open alumina crucibles in air and oxygen atmospheres. Particle size, morphology and the film surfaces were observed from SEM micrographs, which showed that the particles are of sub-micron size, in contrary to the other synthesis methods. EDX analysis were carried out on the same samples to have information about elemental distribution.

ELECTRON EMISSION IN BARIUM TANTALATE IN THE RANGE OF PHASE TRANSITIONS.

B.M.Darinskii and A.P.Lazarev

Voronezh State University, Universitetskaya pl.1
Voronezh, 394693, Russia.

While studying thermostimulated electron emission in ferroelectrics the main attention is concerned with the influence of electron emission current on the state of domain structure in the samples. The influence of surface state has been studied in a considerably less extent. In this work the effect of the state of near-surface layer in paraelectric state on the magnitude of emission current is investigated.

Mechanism of compensation of bound charges in near-surface layer by the free charges captured with traps of various physical nature is concerned. Impurity atoms and impurity complexes, dislocations, surface defects can act as traps. Theoretical investigations of the distribution of bound charges have been performed as well as of electric field and concentration of occupied levels on the opposite surfaces of ferroelectric plate. Electron flows were measured arising after applying of electric field due to electron emission from the sample surface. The probability of electron yield from the surface in dependence on the strength of electric field and direction of polarization on the surface was calculated. It should be noted the difference in emission currents from the opposite surfaces of the polarized sample. The obtained theoretical results are compared with those experimental ones [1]. The nature of maximum in electron emission current in dependence on temperature is also discussed.

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Workshop of the

COST 514
European Concerted Action on Ferroelectric Thin Films

ICMM.CSIC.
Madrid (SPAIN)
4-5 March 1996

CSIC

COST 514 EU ACTION WORKSHOP
"FERROELECTRIC THIN FILMS"

Departamento de Materiales Ferroeléctricos.
Instituto de Ciencia de Materiales de Madrid (ICMM). C.S.I.C.
Cantoblanco. 28049 - Madrid (SPAIN) 4-5 March, 1996

PROGRAM

Monday 4th March

09:30 **Arrival** and collect of documentation.

09:45 **Introductory remarks** by Dr. M. Kosec (by Prof. Nava Setter, Chairwoman of the COST514 Action) and Local Organizers.

SESSION I: Chairwomans: Dr. M. Kosec and L. Pardo.

09:50 - 10:35 Invited talk 1: "**Survey of Developments in Ferroelectric Nonvolatile memories in the USA and Japan**".
Prof. Angus I. Kingon. North Carolina University (U.S.A.)

10:35 - 10:55 Contributed talk 1: "**Ferroelectric characterization of sol-gel modified PbTiO3 Ferroelectric Thin Films**"
Prof. J. Mendiola. ICMM (Spain)

11:00 - 11:30 Coffe Break.

SESSION II: Chairwoman: Dr. M.L. Calzada.

11:30 - 12:15 IT2: "**Ferroelectric Thin Films: Important Applications and Required Material Improvements**"
Dr. W. Wersing. Siemens AG (Germany)

12:15 - 12:35 CT2: "**TEM Studies on Sol-Gel Processed Modified Lead Titanate Thin Films**".
Dr. Etienne Snoeck. CEMES-LOE (France)

12:35 - 12:55 CT3: "**Piezoelectric Measurements and Piezoelectric Fatigue on PZT Thin Films**".
Dr. Andrei Holkin. EPFL (Switzerland)

13:00 - 14:00 Lunch.

SESSION III: Chairman: Prof. S. Lepävuori.

14:00 - 14:30 IT3: "**Measurements of Ferroelectric and Electrostrictive Properties on Lead Titanate Based and PLZT Thin Films** ".
Prof. A. Sternberg. University of Latvia at Riga (Latvia)

14:30 - 14:50 CT4: "**Current Studies on Ferroelectric Thin Films in Stockholm**".
Prof. K.V. Rao. Royal Institute of Technology (Sweden)

14:50 - 15:10 CT5: "**Electrical Properties of Lithium Tantalate Thin Films on Silicon Substrates**"
Drs. Charles-Henry Kohli, P.E. Schmid and F. Levy . EPFL (Switzerland)

15:10 - 15:30 CT6: "**Thermal Annealing of Pt Sputtering and RIE Induced Defects in PZT Ferroelectric Capacitors**"
Dr. Dirk Wouters. IMEC (Belgium)

15:30 - 16:00 Pause

Monday 4th March (cont.)

SESSION IV: Chairman: Dr. W. Wersing.

16:00 - 16:30 CT7: **"Processing Parameters affecting the Properties of Sol-Gel derived Modified Lead Titanate Thin Films"**
Dr. M. Lourdes Calzada. ICMM (Madrid)

16:30 - 16:50 CT8: **"Precursor Chemistry and Properties of Sol-Gel PZT Thin Films"**
Dr. Marija Kosec. Josef Stefan Institute (Slovenia)

16:50 - 17:10 CT9: **"Preparation of PZT Films and Powders by the Sol-Gel Process"**
Prof. A. Macit Özenbaş. Middle East Technical University (TurKey)

17:10 -17:30 CT10: **"Barium Titanate Thin Films: Influence of Precursor Chemistry and Processing on Thin Film Properties"**
Dipl.Phys. S. Hoffmann and Prof. R. Waser. RWTH Aachen (Germany)

Tuesday 5th March.

SESSION V: Chairman: Prof. I. Boyd.

09:30 - 10:15 IT4: **"Laser ablation deposited ferroelectric thin films"**
Prof. A. Safari. Rutgers University (U.S.A.)

10:15 - 10:35 CT11: **"Pulsed laser deposition and electrical characterization of Ca-modified lead titanate thin films"**
Dr. C. Zaldo. ICMM (Spain)

10:35 - 10:55 CT12: **"Factors Controlling the Phase Distribution of PZT Thin Films Prepared by PLD"**
Drs. B.E.Watts and F. Leccabue. MASPEC CNR (Italy)

10:55 - 11:15 Coffe Break.

11:15 - 11:30 **Project Meetings** for the Preparation of yearly report and 15 minutes presentation for each project.

SESSION VI: Chairwoman : Dr. L. Pardo.

11:30 - 12:20 **Presentation** for each project leader:

1.- Reliability of Ferroelectric Thin Films (Dr. M. Kosec)
2.- Materials for a Ferroelectric Capacitor Stack in direct contact to Silicon (Dr. D. Wouters)
3.- Optical and Non-linear Optical properties of Ceramic Thin Films (Dr. B.E. Watts)
4.- Pulsed Laser Ablation Deposition of Ferroelectric Thin Films (Prof. K.V. Rao)
5.- Ferroelectric Thin Films for SAW devices (Dr. L. Pardo)

12:20 - 13:00 **Open Discussion of the State of the Art on Ferroelectric Thin Films. Farewell** to the participants.

13:00 - 14:00 Lunch.

14:30 - 15:30 **Visit to Laboratories.**

PREPARATION OF PZT FILMS AND POWDERS BY THE SOL-GEL PROCESS

MACİT ÖZENBAŞ
Department of Metallurgical Engineering, Middle East Technical University, Ankara,
06531 Turkey

ABSTRACT

The present paper describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

INTRODUCTION

In recent years, preparation and synthesis conditions of uniform and chemically homogeneous particles of ferroelectric ceramics have been investigated by numerous researchers using sol-gel alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely homogeneous precipitation from aqueous solutions.[1] This method involves the reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 75-98°C to produce the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia.

EXPERIMENTAL PROCEDURE

The materials required for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$, and $PbCl_2$, together with some urea. The concentrations studied are given below :

Pb^{+2}	....	0.001 - 0.005 M
Zr^{+4}, Ti^{+4}, Urea	....	0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, together with urea in sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. The resulting PZT precursors were gelled by holding at 90°C for 1 to 2 h while magnetically stirring. The starting pH of the precursors was between 0 and 1. However, the pH gradually increased to 5-5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution. These precipitates were dried at 120°C for 5-6 h in an oven and then they were fired at 350°C, 650°C, and 850°C for 5, 5, and 3 h, respectively, in the oxygen atmosphere to obtain polycrystalline powders.

The substrate materials for the films are silicon (111) wafers and α-Al_2O_3. The coating of the films was accomplished by dipping the substrates into the coating solutions, which were obtained from the precursors used for the powder formation. The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analyses of the bulk gels. The coated films were dried at around 100°C for 10 min. The above process should be repeated in order to increase the thickness of the films. A film of approximately 0.2 μm thick was deposited in a single process and the final film thicknesses determined by SEM were about 1.1-1.2 μm. Finally, the films were annealed at 350°C, 650°C, and 850°C for 3 h in open alumina crucibles in the oxygen atmosphere to obtain crystallization. The heating and cooling rates used were 20°C/min and 1.5°C/min, respectively. The particle size, the morphology and the film surfaces were observed from SEM (Jeol-JSM 6400) micrographs. EDX analyses were carried out on the same samples to give information on the composition of the films.

RESULTS AND DISCUSSION

The resulting crystal structure of sol-gel derived PZT thin films was highly sensitive to both the initial chemical composition and heat treatment temperature. In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. Sol-gel derived powder samples crystallized at temperatures approximately 50°C lower than corresponding thin film samples. Consistent with the literature, the development of the initial pyrochlore phase was observed during the thermal processing of thin films. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent.[2,3] In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analyses showed that films of 1.1-1.2 μm thickness were polycrystalline with no preferred crystallographic orientation (Fig. 1).

For the observation of powders, small amounts of the suspensions were rapidly dried by heating on common SEM sample holders, the surface of which had additionally been polished to less than 0.5μm surface roughness.[4] Figure 2.a shows the particles of PZT composition obtained by using urea, which yielded particle sizes from submicron range to a few microns. The particles of the same composition obtained without the use of urea were about 50-100 μm in size (Figure 2.b). The use of the homogeneous precipitation process leads to micron-sized particles with high homogeneity and possibly gives films with better physical properties.

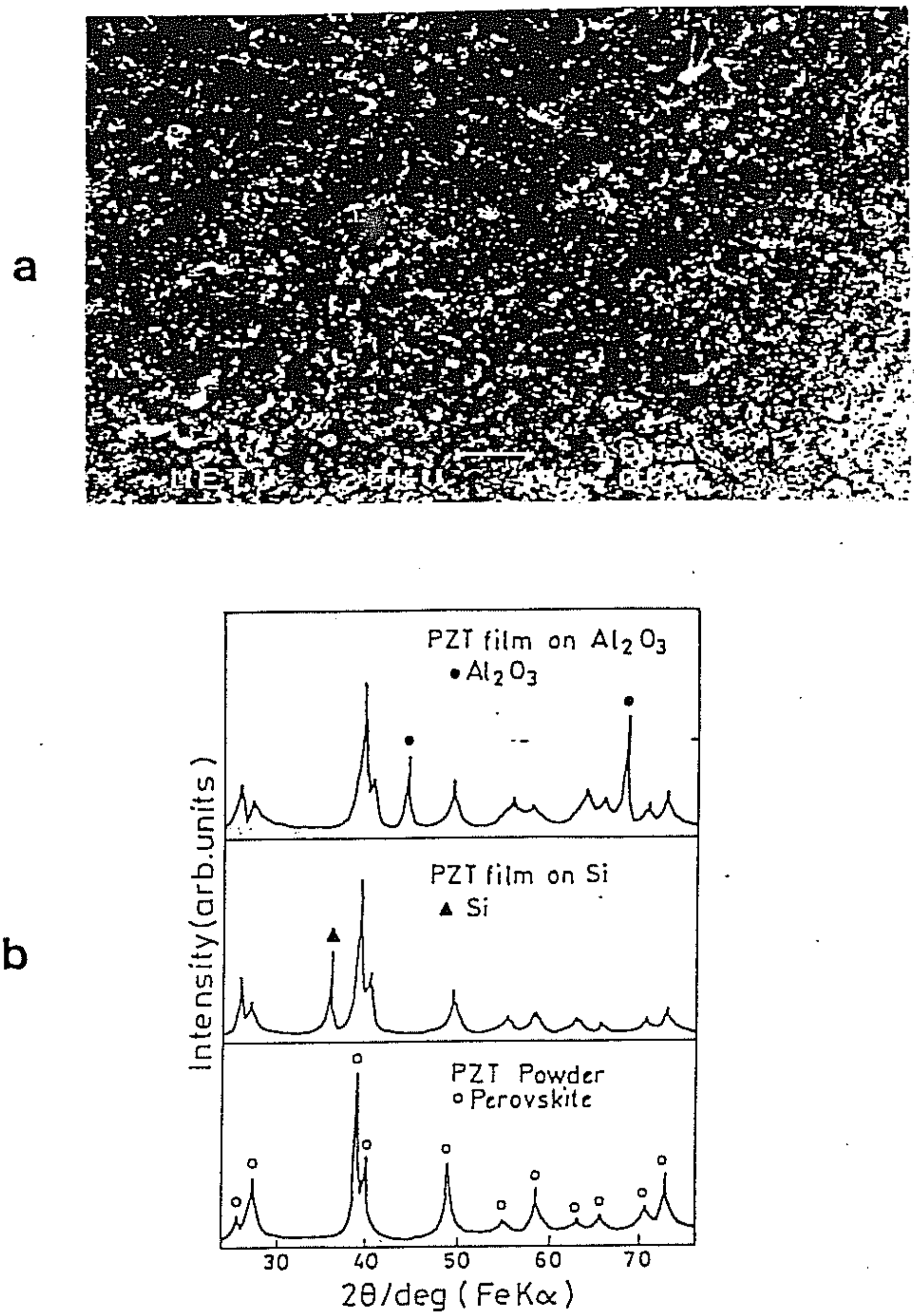
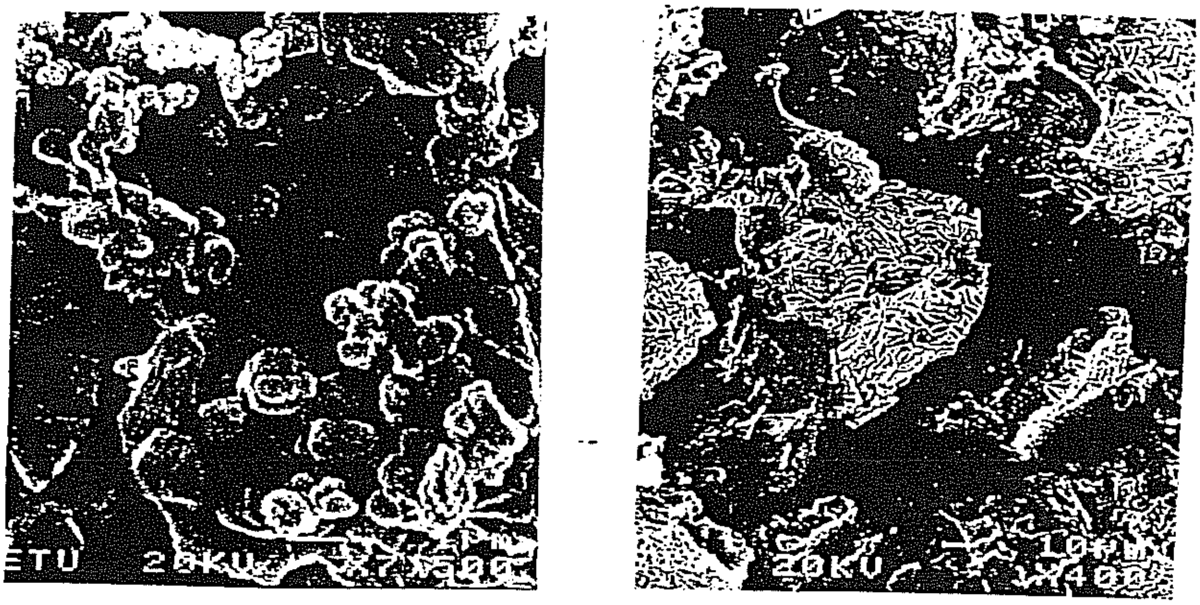


Figure 1. (a) Scanning electron micrograph of the PZT film surface on alumina substrate, heat treated at 850°C for 3 h, (b) XRD patterns of the films on alumina and silicon substrates.

Conversion of the precipitated amorphous powders to the PZT oxide phase was evaluated by X-ray diffraction. XRD studies show that the crystallization started around 350°C. Heat treatment at 650°C decreased the amount of pyrochlore phase and finally at 850°C, the sample was all perovskite phase. This temperature is especially important for lead-containing systems to avoid the PbO loss problem during heat treatment.[5] The crystal structure appeared to transform from pseudocubic to tetragonal with increasing temperature, and the original composition was slightly to the tetragonal side of the morphotrophic phase boundary.[6] The enhanced definition of tetragonal splitting, with increased intensity at higher temperatures, indicates a greater degree of crystallinity for material heat-treated at these temperatures. The lattice parameters for the gel-derived powders agree with those of the sintered samples, which indicates that the chemical composition of the gel-derived powders does not deviate much from that of the starting solutions.[7]



a

b

Figure 2. (a) Scanning electron micrograph of sol-gel derived PZT particles obtained by using urea, (b) Scanning electron micrograph of sol-gel derived PZT particles obtained without the use of urea.

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PI-13 **Structural Characterization of Sol-Gel PZT Thin Films**
S.A. Impey, R.W. Whatmore, *Z. Huang, **N.M. Shorrocks, and **A. Patel
Cranfield University, ENGLAND & *University of Essex, ENGLAND & **GEC Marconi Materials Technology, ENGLAND

PI-14 **Thin Film Deposition of Barium Strontium Titanate (BST) by Metallo-Organic Decomposition (MOD) Technique**
P. Jana and R.K. Pandey
Texas A&M University, USA

PI-15 **Effect of DC Bias Field on the Dielectric Properties**
H. Khemakhem, J. Ravez, and *A. Daoud
Institut de Chimie de la Matiere Condensee de Bordeaus, FRANCE & *Laboratoire de l'Etat Solide, FRANCE

PI-16 **Influence of Different Lead Precursors on the Microstructure and Properties of Sol-Gel Thin Films**
M. Kosec, U. Delalut, V. Bobnar, and G. Drazic
Jozef Stefan Institute, SLOVENIA

PI-17 **Study of DC Conduction Behavior of Barium Strontium Titanate Thin Films**
S.B. Krupanidhi
Indian Institute of Science, INDIA

PI-18 **Electrical Characterization of Sol-Gel Derived PZT and PLZT Thin Films**
R. Kurchania and S.J. Milne
University of Leeds, UNITED KINGDOM

PI-19 **Ferroelectric Field Effect in (La,Sr)CoO$_3$/Pb(Zr,Ti)O$_3$ Heterostructure**
J. Lee and S. Kim
Sung Kyun Kwan University, KOREA

PI-20 **Anomalous Imprint Characteristics of Bi$_4$Ti$_3$O$_{12}$ Thin Films Grown by Pulsed Laser Deposition**
J. Lee, B.H. Park, T.W. Noh, *W. Jo, and *C-Y. Kim
Sung Kyun Kwan University, KOREA & *Seoul National University, KOREA

PI-21 **Coherent Coupling in Ferroelectric Superlattices**
S. Li, J.A. Eastman, J. Vetrone, *R.E. Newnham, and *L.E. Cross
Argonne National Laboratory, USA & *Pennsylvania State University, USA

PI-22 **Preparation of Pb(Zr,Ti)O$_3$ Thin Films on TiNi SMA Substrates by Sol-Gel Processing**
X.S. Li, Q.F. Liu, J.R. Cheng, and Z.Y. Meng
Shanghai University, CHINA

PI-23 **Rejuvenation of Fatigued Sol-Gel Derived Ferroelectric PZT Thin Films**
Y. Liu and P.P. Phule
University of Pittsburgh, USA

PI-24 **PZT Thin Film Preparation on Pt/Ti Electrodes by RF Magnetron Sputtering**
D.X. Lu, E.M.W. Wong, E.Y.B. Pun, and *Z.Y. Lee
City University of Hong Kong, HONG KONG & *Huazhong University, CHINA

Electron Cyclotron Resonance (ECR) Sputtering
H. Maiwa and *N. Ichinose
Shonan Inst. of Technology, JAPAN & *Waseda University, JAPAN

PI-26 **Microstructure and Ferroelectric Properties of Sol-Gel PZT Thin Films on Nickel Alloy Electrode for Use With Soda-Lime Glass Substrate**
T. Ogawa, N. Ujiie, and K. Hukuta
Shizuoka Institute of Science & Technology, JAPAN

PI-27 **Improvement in Fatigue Properties of Ferroelectric Bi$_4$Ti$_3$O$_{12}$ Thin Films by Heat Treatment in O$_2$ Gas at High Pressure**
S. Okamura, *A. Kakimi, *S. Ando, *Y. Yagi, K. Mori, and T. Tsukamoto
Science University of Tokyo in Yamaguchi, JAPAN & *Science University of Tokyo, JAPAN

PI-28 **Preparation of PbZr$_{0.5}$Ti$_{0.5}$O$_3$ Films and Powders by the Sol-Gel Process**
M. Ozenbas
Middle East Technical University, TURKEY

PI-29 **Temperature Dependent Fatigue in Ferroelectric PZT Thin Films**
E.N. Paton, S.A. Mansour, and A. Bement, Jr.
Purdue University, USA

PI-30 **Dielectric Anomalies in Epitaxial Ferroelectric Thin Films: Possible Way to DRAM**
N.A. Pertsev
RUSSIA

PI-31 **Ferroelectric Thin Films with Polarization Gradients Normal to the Growth Surface**
N.W. Schubring, J.V. Mantese, A.L. Micheli, and A.B. Catalan
General Motors R&D Laboratories, USA

PI-32 **Electrical Properties of (Pb,Zr)TiO$_3$ Thin Films on Ir and IrO$_2$ Electrodes by MOCVD**
M. Shimizu, *H. Okino, *H. Fujisawa, and *T. Shiosaki
Himeji Institute of Technology, JAPAN & *Kyoto University, JAPAN

PI-33 **Structural and Ferroelectric Properties of R.F. Magnetron Sputtered SrBi$_2$Ta$_2$O$_9$ Thin Films**
T.K. Song, J.-K. Lee, and H.J. Jung
Korea Institute of Science & Technology, KOREA

PI-34 **Processing and Properties of In-Situ Pulsed Laser Deposited PMN-PT Thin Films**
C. Tantigate and A. Safari
Rutgers University, USA

PI-35 **Dielectric Property Evaluation of Barium Strontium Titanate Thin Films Prepared by a Sol-Gel Technique**
D.M. Tahan, A. Safari, and L.C. Klein
Rutgers University, USA

PI-36 **Dielectric and Ferroelectric Characterization of Sol-Gel Derived Ca-Doped PbTiO$_3$ Thin Films**
G. Teowee, K. McCarthy, C.D. Baertlein, E.K. Franke, J.M. Boulton, *T.P. Alexander, and *D.R. Uhlmann
Donnelly Corporation, USA & *University of Arizona, USA

P1-27

IMPROVEMENT IN FATIGUE PROPERTIES OF FERROELECTRIC $Bi_4Ti_3O_{12}$ THIN FILMS BY HEAT TREATMENT IN O_2 GAS AT HIGH PRESSURE

Soichiro Okamura, Atsushi Kakimi, Shizutoshi Ando[1], Yukie Yagi, Katsumi Mori, and Takeyo Tsukamoto[1]
Science University of Tokyo in Yamaguchi, 1-1-1 Daigaku-dori, Onoda, Yamaguchi 756, Japan
[1]Science University of Tokyo, 1-3 Kagurazaka, Shinjyuku-ku, Tokyo 162, Japan

We fabricated ferroelectric $Bi_4Ti_3O_{12}$ thin films using metal organic acids as starting materials. Substrates were spin-coated with the metal organic acids and calcined at 500°C for 5 min. This procedure was repeated several times to control the thickness of films. Then, the spin-coated films were heat-treated at 800°C for 30 min in O_2 gas with the pressures ranging from 0.1 to 0.4 MPa. In any conditions, ferroelectric $Bi_4Ti_3O_{12}$ thin films with c-axis orientation were obtained. While remanent polarization P_r of the film heat-treated at 0.1 MPa was estimated to be 1.2 $\mu C/cm^2$ and reduced to half of the initial value after polarization reversal at 10^7 cycles, one of the film heat-treated at 0.4 MPa was estimated to be 2.1 $\mu C/cm^2$ and constant up to 10^9 cycles. Other electrical properties also were improved by heat treatment in O_2 gas at high pressure.

P1-28

PREPARATION OF $PbZr_{0.5}Ti_{0.5}O_3$ FILMS AND POWDERS BY THE SOL-GEL PROCESS

Macit Ozenbas
Middle East Technical University, Department of Metallurgical and Materials Engineering, Ankara, Turkey

The present work describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea $[(NH_2)_2CO]$. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The process involved the addition of stock solutions in proper amounts to from the desired compound at the end, together with urea in sufficient water to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. It is observed that the particles of PZT composition obtained by using urea yielded particle sizes from submicron range to a few microns. The coating of the films was carried out on alumina and silicon substrates by dipping them into the coating solutions, which were obtained from the precursors used for the powder formation. The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analysis of the bulk gels. The resulting crystal structure of sol-gel derived PZT films was highly sensitive to both the initial chemical composition and heat treatment temperature. In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent. In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analysis showed that films of 1.1-1.2 μm thickness were polycrystalline with no preferred crystallographic orientation.

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PREPARATION OF $Pb(Zr,Ti)O_3$ THIN FILMS AND POWDERS BY THE SOL-GEL PROCESS

MACIT ÖZENBAS and ÜMIT ERGIN
Dept. of Metallurgical Eng., Middle East Technical University, Ankara, Turkey

(Received July 3, 1995; in final form January 16, 1996)

Abstract The present paper describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

INTRODUCTION

The conditions for the preparation and synthesis of uniform and chemically homogeneous particles of ferroelectric ceramics have been investigated, in recent years, by numerous researchers using sol-gel alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely homogeneous precipitation from aqueous solutions.[1] This method involves the reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 75-98°C, producing the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, n situ, is used as the ligand source for ammonia.

EXPERIMENTAL PROCEDURE

The materials required for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$, and $PbCl_2$, together with some urea. The concentrations investigated are given below :

Pb^{+2} .... 0.001 - 0.005 M
Zr^{+4}, Ti^{+4}, Urea .... 0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the esired compound at the end, together with urea in sufficient water to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. The resulting PZT precursors were gelled by holding at 90°C for 1 to 2 h while magnetically stirring. The starting pH of the precursors was between 0 and 1. However, the pH gradually increased to 5-5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution. These precipitates were dried at 120°C for 5-6 h in an oven and then fired at 350°C, 650°C, and 850°C for 5, 5, and 3 h, respectively, in an oxygen atmosphere to obtain polycrystalline powders.

The substrate materials for the films are silicon (111) wafers and α-Al_2O_3. The coating of the films was accomplished by dipping the substrates into the coating solutions, which were obtained from the precursors used for the powder formation. The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analyses of the bulk gels. The coated films were dried at around 100°C for 10 min. The above process may be repeated in order to increase the thickness of the films. A film of approximately 0.2 μm thick was deposited in a single process and the final film thicknesses determined by SEM were about 1.1-1.2 μm. Finally, the films were annealed at 350°C, 650°C, and 850°C for 3 h in open alumina crucibles in an oxygen atmosphere to obtain crystallization. The heating and cooling rates used were 20°C/min and 1.5°C/min, respectively. The particle size, the morphology and the film surfaces were observed from SEM (Jeol-JSM 6400) micrographs. EDX analyses were carried out on the same samples to give information on the composition of the films.

RESULTS AND DISCUSSION

For the observation of powders, small amounts of the suspensions were rapidly dried by heating on common SEM sample holders, the surface of which had additionally been polished to less than 0.5μm surface roughness.[2] Figure 1.a shows the particles of PZT composition obtained by using urea, which yielded particle sizes from submicron range to a few microns. The particles of the same composition obtained without the use of urea were about 50-100 μm in size. The use of the homogeneous precipitation process leads to micron-sized particles with high homogeneity and possibly gives films with better physical properties.

Conversion of the precipitated amorphous powders to the PZT oxide phase was evaluated by X-ray diffraction. Figure 1.b shows that the crystallization started around 350°C. Heat treatment at 650°C decreased the amount of pyrochlore phase and finally at 850°C, the sample was all perovskite phase. This temperature is especially important for lead-containing systems to avoid the PbO loss problem during heat treatment.[3] The crystal structure appeared to transform from pseudocubic to tetragonal with increasing temperature, and the original composition was slightly to the tetragonal side of the morphotrophic phase boundary.[4] The enhanced definition of tetragonal splitting, with increased intensity at higher temperatures, indicates a greater degree of crystallinity for material heat-treated at these temperatures. The lattice parameters for the gel-derived powders agree with those of the sintered samples, which indicates that the chemical composition of the gel-derived powders does not deviate much from that of the starting solutions.[5]

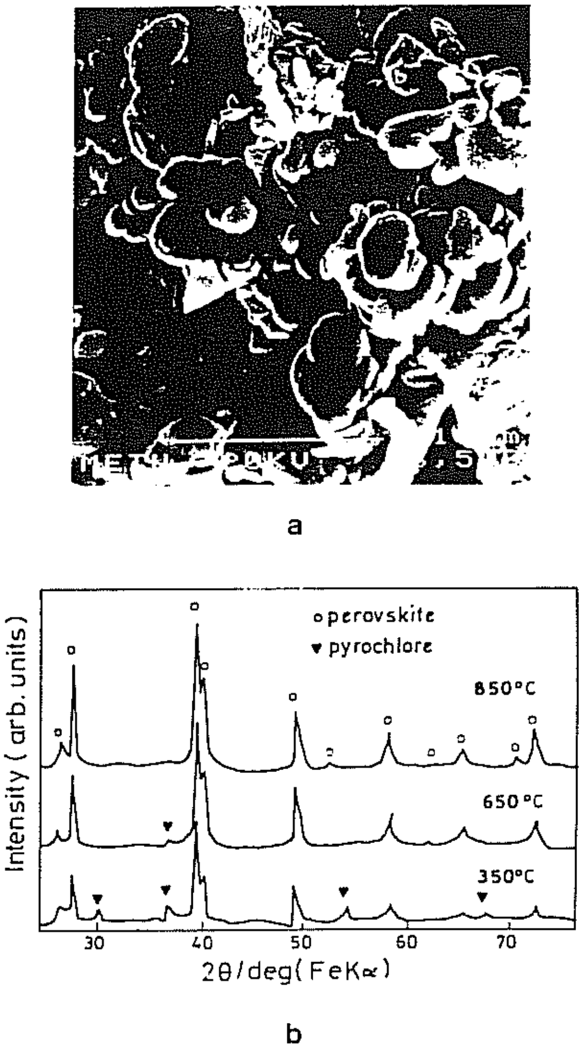
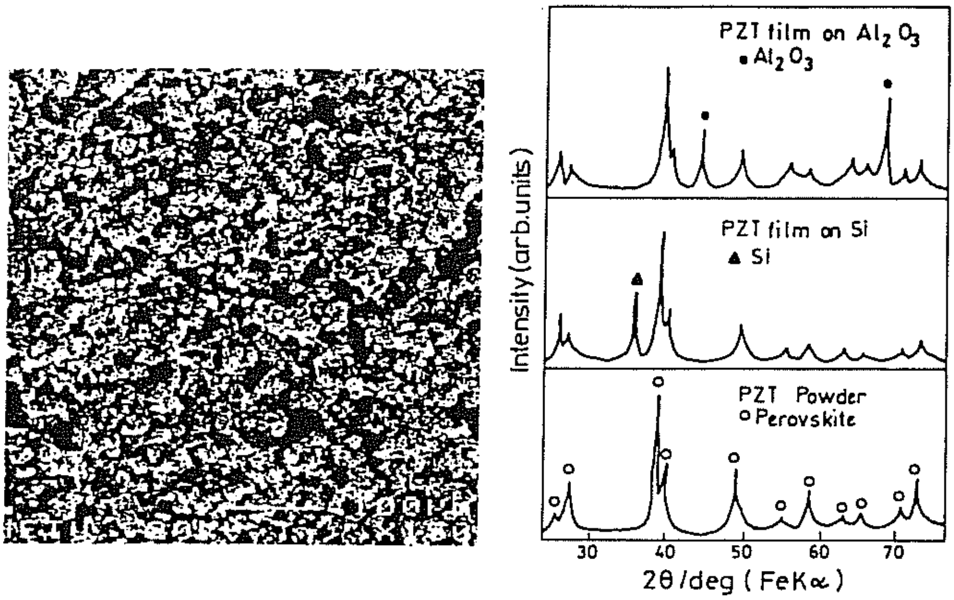


FIGURE 1 (a) Scanning electron micrograph of sol-gel derived PZT particles obtained by using urea. (b) XRD patterns of PZT powders for different heat treatment temperatures.

The resulting crystal structure of sol-gel derived PZT thin films was highly sensitive to both the initial chemical composition and heat treatment temperature. In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. Sol-gel derived powder samples crystallized at temperatures approximately 50°C lower than corresponding thin film samples. Consistent with the literature, the development of the initial pyrochlore phase was observed during the thermal processing of thin films. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent.[6,7] In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analyses showed that films of 1.1-1.2 μm thickness were polycrystalline with no preferred crystallographic orientation (Fig. 2).



a b

FIGURE 2 (a) Scanning electron micrograph of the PZT film surface on alumina substrate, heat treated at 850°C for 3 h. (b) XRD patterns of the films on alumina and silicon substrates.

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S. Ü. ERGİN,
M. ÖZENBAŞ,
C. TAN

Preparation and Characterization of Ferroelectric Thin Films

Department of Metallurgical Engineering,
Middle East Technical University,
Ankara - Turkey

Introduction

Ferroelectric ceramic thin films are non-metallic solid thin films that possess spontaneous polarization which can be reversed by an external electric field. Due to these unique properties, ferroelectric materials are used in various applications such as capacitors, piezoelectric materials (transducers), pyroelectric detectors, electro-optic materials, thermistors and dielectrics. The objective of the study is to promote a research for the preparation of ferroelectric thin films using homogeneous precipitation from aqueous solutions in the presence of urea $[(NH_2)_2CO]$. The investigation of the films and film/substrate interfaces by SEM and TEM can provide useful data for the interpretation of ferroelectric properties.

Materials and Methods

The required materials for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$ and $PbCl_2$, together with some urea. The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, and urea to sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solution. The resulting PZT solutions were gelled by holding at 90°C for 1 to 2 hours while magnetically stirring. The precipitate was redissolved by adjusting the solution pH to yield gels of $Pb(Zr,Ti)O_3$. Particle size and morphology were observed from SEM micrographs, which showed that the particles are of sub-micron size. EDX analysis were carried out on the same samples to have information about elemental distribution.

Results and Discussion

The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of IR spectra of the films. The peaks associated with the residual organics become weak with increasing heat treatment temperature and finally disappear over 400°C, indicating that the residual organics can be eliminated by heat treatment over 400°C. The crystallization process of the films was found to be dependent on the substrates used. Films coated on Si substrates showed that the perovskite phase is already dominant at 550°C, while heat treatment over 600°C is necessary for the films on sapphire substrates. In other words, the perovskite phase precipitates more easily on Si than on sapphire substrates.

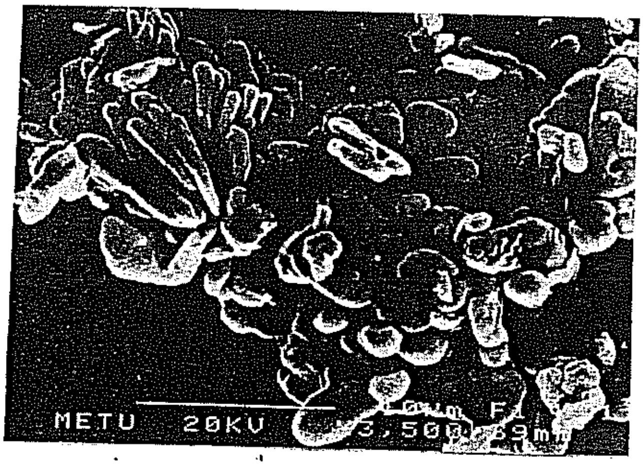

Figure 1. SEM micrograph of PZT powders.

ULUSLARARASI KATILIMLI
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ELEKTRON MİKROSKOPİ KONGRESİ

BİLDİRİLER KİTABI

PROCEEDINGS

OF
WITH INTERNATIONAL PARTICIPATION
13th NATIONAL
ELECTRON MICROSCOPY CONGRESS

EDİTÖRLER / EDITED BY
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ANKARA

SOL-GEL PROCESSING AND CHARACTERIZATION OF FERROELECTRIC $Pb(Zr,Ti)O_3$ FILMS

Macit ÖZENBAŞ and Nilgün TURHAN

Middle East Technical Univ., Metallurgical and Materials Eng. Dept., Ankara, Türkiye

ABSTRACT

The present paper describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and Pt-coated silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

Keywords: PZT, Ferroelectric films, Sol-gel processing.

1. INTRODUCTION

Ferroelectric thin films are non-metallic solid thin films that possess spontaneous polarization which can be reversed by an external electric field. Due to these unique properties, they are used as capacitors, transducers, pyroelectric detectors, electro-optic materials, thermistors, etc. The conditions for the preparation and synthesis of uniform and chemically homogeneous particles of ferroelectric ceramics have been investigated, in recent years, by numerous researchers using sol-gel alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely homogeneous precipitation from aqueous solutions [1]. This method involves the reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 85-95°C, producing the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia.

2. EXPERIMENTAL PROCEDURE

The materials required for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$, and $PbCl_2$, together with some urea. The concentrations investigated are given below :

Pb^{+2}	0.03 - 0.05 M
Zr^{+4},	0.4 M
Ti^{+4}	9.11 M
Urea	0.01 - 0.05 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, together with urea in sufficient water to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. The resulting PZT precursors were gelled by holding at 90-95°C for 7 to 10 h while magnetically stirring. The starting pH of the precursors was between 0 and 1. However, the pH gradually increased to 4.5 to 5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution. These precipitates were dried at 120°C for 5-6 h in an ambient atmosphere and then fired at 350°C, 550°C, and 850°C for 5 hours in an oxygen atmosphere to obtain polycrystalline powders.

The substrate materials for the films are silicon (111) wafers and α-Al_2O_3. The coating of the films was accomplished by dipping the substrates into the coating solutions, which were obtained from the precursors used for the powder formation. The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analyses of the bulk gels. The coated films were dried at around 100°C for a few hours. The above process may be repeated in order to increase the thickness of the films. A film of approximately 0.2 μm thick was deposited in a single process and the final film thicknesses determined by SEM were about 1.1-1.2 μm. Finally, the films were annealed at 350°C, 550°C, and 850°C for 5 h in open alumina crucibles in an oxygen atmosphere to obtain crystallization. The heating and cooling rates used were 20°C/min and 1.5°C/min, respectively. The particle size, the morphology and the film surfaces were observed from SEM (Jeol-JSM 6400) micrographs. EDX analyses were carried out on the same samples to give information on the composition of the films.

3. RESULTS AND DISCUSSION

For the observation of powders, small amounts of the suspensions were rapidly dried by heating on common SEM sample holders, the surface of which had additionally been polished to less than 0.5 μm surface roughness [2]. Figure 1.a shows the particles of PZT composition obtained by using urea, which yielded particle sizes from submicron range to a few microns. The particles of the same composition obtained without the use of urea were about 50-100 μm in size (Figure 1.b). The use of the homogeneous precipitation process leads to micron-sized particles with high homogeneity and gives films with better physical properties. Heterogeneities in the chemical distribution can degrade the electrical performance characteristics .

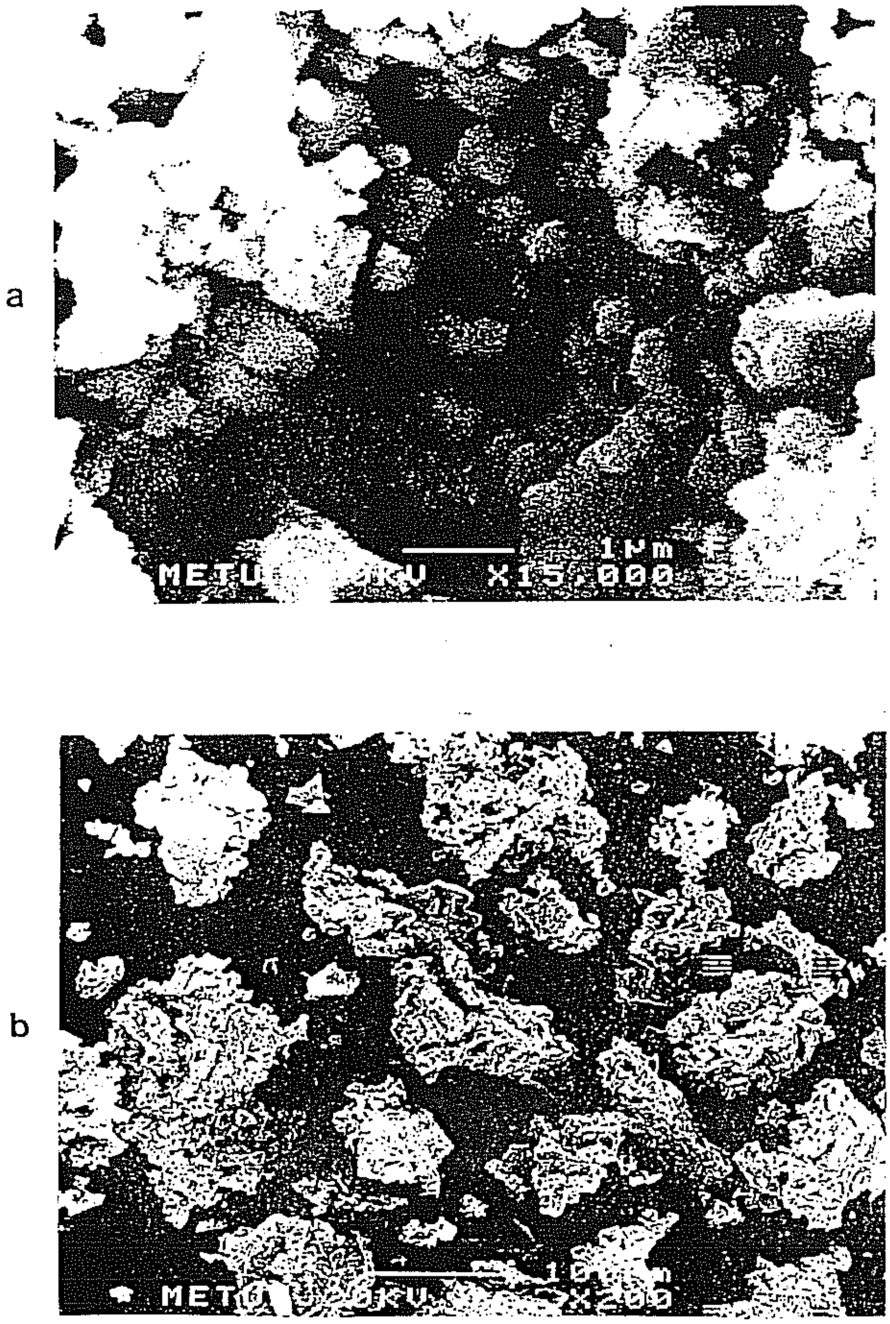

Figure 1. **a.** PZT powder prepared by using urea, annealed at 850°C for 5 h having spherical and fine particle size.
b. PZT powder prepared without using urea.

Conversion of the precipitated amorphous powders to the PZT oxide phase was evaluated by X-ray diffraction. XRD studies show that the crystallization started around 350°C. Heat treatment at 550°C decreased the amount of pyrochlore phase and finally at 850°C, the sample was all perovskite phase. This temperature is especially important for lead-containing systems to avoid the PbO loss problem during heat treatment [3]. The crystal structure appeared to transform from pseudocubic to tetragonal with increasing temperature, and the original composition was slightly to the tetragonal side of the morphotrophic phase boundary [4]. The enhanced definition of tetragonal splitting, with increased intensity at higher temperatures, indicates a greater degree of crystallinity for material heat-treated at these temperatures. The lattice parameters for the gel-derived powders agree with those of the sintered samples, which indicates that the chemical composition of the gel-derived powders does not deviate much from that of the starting solutions [5].

The resulting crystal structure of sol-gel derived PZT thin films was highly sensitive to both the initial chemical composition and heat treatment temperature. In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. Sol-gel derived powder samples crystallized at temperatures approximately 50°C lower than corresponding thin film samples. Consistent with the literature, the development of the initial pyrochlore phase was observed during the thermal processing of thin films. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent [6,7]. In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analyses showed that films of 1.1-1.2 μm thickness were polycrystalline with no preferred crystallographic orientation (Figure 2).

Table 1 summarizes the results of EDX analyses carried out all through this work. Only some representatives had been chosen from a set of samples, and these analyses are point analyses on the film surfaces. For this reason the values on the table 1 show some variations from stoichiometry.

What were achieved and observed in this study are as follows:

- PZT powders and films of desired stoichiometry, composition, particle size and morphology were prepared.
- Urea addition was resulted in fine, mono sized (<1μm), homogeneously distributed particles, and correspondingly thinner films.
- The films prepared by no urea addition showed surface roughness and were not dense enough.
- The suitable annealing temperature and time for both PZT powders and films was determined to be 5 hours at 850°C
- IR analyses did not show the presence of any impurities in the samples heat treated as in the previous conclusion.
- Wetting characteristics of the films were better on alumina and Pt-coated Si substrates than that on bare Si substrates.

Table 1. EDX results of the studies for PZT powder and film preparation (point analyses with atom %).

PZT Powder	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Ratio
No Heat Treatment	32.86	19.55	15.07	32.52	1:0.59:0.49
350°C, 5 hr.	37.96	15.86	19.64	26.54	1:0.42:0.52
550°C, 5 hr	40.94	24.82	24.03	10.21	1:0.61:0.57
750°C, 5 hr	47.62	18.33	21.12	12.93	1:0.38:0.44
850°C, 3 hr	49.88	23.83	26.29	-	1:0.48:0.53
850°C, 5 hr	45.59	27.11	27.30	-	1:0.59:0.60
350°C, 5 hr (without urea)	49.79	22.93	27.28	-	1:0.46:0.55
PZT Film/Al_2O_3 substrate	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Ratio
No Heat Treatment	41.73	14.00	24.19	20.10	1:0.33:0.58
850°C, 3 hr	39.17	20.22	26.45	14.16	1:0.52:0.68
850°C, 5 hr	48.79	24.46	31.75	-	1:0.50:0.65
850°C, 5 hr (Ti-rich phase)	21.71	27.89	50.41	-	1:1.28:2.32
850°C, 5 hr (without urea)	38.79	30.28	30.93	-	1:0.78:0.80
PZT Film/Pt-coated Si sub.	Pb (atom %)	Zr (atom %)	Ti (atom %)	Cl (atom %)	Pb:Zr:Ti Ratio
No Heat Treatment	44.66	14.73	22.01	18.60	1:0.33:0.49
850°C, 3 hr	35.79	28.94	22.81	12.46	1:0.81:0.64
850°C, 5 hr	42.61	24.96	32.43	-	1:0.59:0.76
850°C, 5 hr (without urea)	42.74	27.19	30.07	-	1:0.64:0.70

Figure 2. PZT film on Pt-coated Si substrate prepared by using urea and annealed at 850°C for 5 hours.

Acknowledgement

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ABSTRACTS

ceramics. We have also quantified the effects of porosity on mechanical properties. Of particular interest in our study is the use of TiN as a container material for pyrochemical processes in which the material is exposed to corrosive molten salts at temperatures of ≈800°C. Because of the difficulty in fabricating large process vessels from bulk TiN, graphite specimens coated with TiN (≈10 mm thick) were prepared by chemical vapor deposition. The thermal expansion of graphite and the coatings were closely matched to give thermal shock resistance. Pin-pull adhesion tests were used to measure failure stress, and the data were analyzed by Weibull statistics. Corrosion tests on TiN-coated graphite in molten salts show that graphite coated with TiN is very promising.

*Work supported by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under contract W-31-109-Eng-38.

W6.42

EPITAXIAL ZnO PIEZOELECTRIC FILMS FOR RF FILTERS.

Yicheng Lu, Nuri Emanetoglu, Shaohua Liang, Ying Liu, Department of Electrical and Computer Engineering, Rutgers University, Piscataway, NJ; Chandrasekhar Gola, William Mayo, Department of Ceramics, Rutgers University, Piscataway, NJ.

ZnO has high piezoelectric coupling coefficient and acoustic velocity; therefore, it is an attractive material candidate for high frequency and low loss filters. Piezoelectric ZnO thin film based RF devices offer the advantages such as low power consumption, circuit miniaturization and cost reduction through integration with main stream MMIC technology. We report CVD growth of epitaxial ZnO thin films on C- and R-sapphire substrates. X-ray diffraction techniques have been used to study the crystallinity and orientation of the films, as well as the epitaxial relationship between the films and the substrate. High-resolution cross-sectional TEM reveals the atomically sharp interface structure. As-grown the ZnO films exhibit dominate n-type conductivity due to the oxygen vacancies. The excellent piezoelectricity has been achieved through a multi-step Li diffusion under oxygen ambient. A testing transducer with 10-micron wavelength has been fabricated. It shows the harmonic SAW modes up to 1.5 GHz with low insertion loss.

W6.43

A COMPARISON OF FERROELECTRIC THIN FILMS PREPARED BY SOL-GEL AND PHOTOCHEMICAL METHODS.

R.H. Hill, S.L. Blair, Y. Shi, and I. Yaroslavsky, Department of Chemistry, Simon Fraser University, Burnaby, BC CANADA.

Lead zirconate titanate (PZT) and barium strontium titanate (BST) thin films have potential applications in nonvolatile memory devices, infrared sensors and microactuators. This paper will describe the deposition of PZT and BST films using two different methods. The two methods are sol-gel deposition and photochemical deposition from amorphous films of inorganic complexes. The new photochemical method as well as the known sol-gel method provide relatively easy composition control to fabricate PZT and BST thin films for device applications. In these studies we investigated the film quality, crystalline orientation as well as some of the electrical properties of the deposited films under various annealing conditions. The resultant films were analyzed by x-ray diffraction and optical microscopy. Under identical annealing conditions, both methods produced tetragonal PZT and BST films on various substrates. A comparison of the photochemical- and sol-gel methods demonstrated that we can receive the tetragonal phase of PZT or BST using either method. The photochemical method requires a shorter annealing time at 650°C to produce the tetragonal phase of PZT (5 min) than the sol-gel method (1-5 hr). However, both methods produce films of good crystallinity with longer annealing times. Lead oxide has a high volatility under the annealing conditions used. Therefore, for sol-gel preparation, excess lead reagent is required to compensate for Pb losses. This decreases the quality of PZT films deposited using the sol-gel method.

W6.44

SOL-GEL PROCESSING AND CHARACTERIZATION OF FERROELECTRIC $Pb(Zr,Ti)O_3$ FILMS AND POWDERS.

Macit Ozenbas, Dept of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, TURKEY.

In this study, ferroelectric $Pb(Zr,Ti)O_3$ films and powders were prepared from metal chlorides using sol-gel processing method. For powders; homogeneous precipitation from aqueous solution and for films; dip coating just before precipitation was applied in the presence of urea, $[(NH_2)_2CO]$. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and Pt-coated silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films. Characterization of the films and powders were carried out primarily by XRD and SEM/EDX. The particle size and morphology, and film surfaces were observed during SEM studies, while compositions of the films and powders were investigated by EDX analyses. Phases formed upon annealing were determined by XRD of the samples at several stages of annealing. In order to accurately determine the impurities remained in the powder samples, IR spectroscopic analyses were carried out. Both the films and powders were stoichiometric and completely crystallized into perovskite phase after annealing for 5 hours at 850°C. For annealing temperatures between 350 and 650°C, perovskite, pyrochlore, lead titanate, and for those between 650 and 850°C, pyrochlore and perovskite phases were observed. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent. The PZT powders had homogeneously distributed, fine particle sizes and morphology; however, the films prepared were partly deviated from compositional homogeneity. The films have better wetting characteristics on alumina and Pt-coated Si substrates than that on bare silicon substrates. XRD analyses showed that films of 1.1-1.2 μm thickness were polycrystalline with no preferred crystallographic orientation.

W6.45

SOL-GEL DERIVED $YMnO_3$ THIN FILMS.

K. McCarthy, G. Teowee, F.S. McCarthy, Donnelly Corporation, Tucson, AZ; D. Davis and D.R. Uhlmann, Dept of Materials Science and Engineering, University of Arizona, Tucson, AZ.

There has been much interest on ferroelectric thin films especially for non-volatile memories and ultra high density DRAM applications. These films typically consisted of lead zirconate titanate (PZT) with oxide contacts or layered perosvkite such as $SrBi_2Ta_2O_9$. Recently there has been reports of sputtered $YMnO_3$ films which exhibit a single polarization axis and does not contain any voltaile species such as Pb or Bi. Single crystal $YMnO_3$ exhibits satisfactory polarization and low coercive field. In this study, the dielectric and ferroelectric properties of sol-gel derived $YMnO_3$ films prepared on platinized Si wafers will be discussed especially with regards to the firing conditions and hexagonal phase development

W6.46

ELECTRICAL CHARACTERISTICS OF BORON-ADDED $(Ba,Sr)TiO_3$ THIN FILMS FABRICATED BY SOL-GEL METHOD.

Soo-Ik Jang and H.M. Jang, Department of Materials Science and Engineering, and Laboratory for Physics/Chemistry of Dielectric Materials, Pohang University of Science and Technology (POSTECH), Pohang, SOUTH KOREA.

Thin films of $Ba_xSr_{1-x}TiO_3$ (BST with x=0.5) were prepared on $RuO_2/Ru/SiO_2/Si$ substrates by the sol-gel method using Ba-,Sr-, and Ti-alkoxides as starting precursors. Boron-alkoxide was intentionally introduced to induce a liquid-phase sintering for reducing the temperature for the crystallization and establishing a better microstructure. AFM micrographs showed that the BST thin film with a smooth surface roughness and a crack-free uniform microstructure was gradually developed with increasing boron concentration. The 250nm-thick films fired at 700°C exhibited the dielectric constant values of 420, 360, 190 (at 1MHz) for pure, 5mol%, and 10mol% boron-addition, respectively. A vitreous B_2O_3 phase (ϵ_r=3) in the grainboundary was considered to reduce the relative dielectric permittivity. The leakage current density of the 10mol% boron-added film was about $2.6\times10^{-7}A/cm^2$ at 1V and decreased with increasing boron content. The leakage current at the applied voltage higher than 1V showed a linear variation of log J with $E^{1/2}$ at room temperature, suggesting that the Schottky emission was the dominant conduction process.

SESSION W7: MOCVD OF ELECTRONIC CERAMICS III - PRECURSORS

Chair: John J. Sullivan
Wednesday Morning, December 3, 1997
Salon C/D (M)

8:30 AM *W7.1

PRECURSORS FOR VAPOR DEPOSITION OF PHOSPHORS FOR ELECTROLUMINESCENT FLAT PANEL DISPLAYS.

William S. Rees Jr, Oliver Just, Henry A. Luten, and David Otway; Georgia Institute of Technology, School of Chemistry and Biochemistry, School of Materials Science and Engineering and Molecular Design Institute, Atlanta, GA.

One challenge for the high brightness, low power consumption, full color electroluminescent (EL) flat panel displays is the blue component of the spectrum. One leading candidate for this composition is SrS:Ce. Earlier efforts in atomic layer epitaxy (ALE) of this EL material relied on the tetramethylheptanedionate derivatives

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COST 514
on

"FERROELECTRIC CERAMIC THIN FILMS"

List of projects

B1: Reliability of Ferroelectric thin Films	Dr.ir. Dirk Wouters IMEC, Division MAP-ARS Kapeldreef 75 B-3001 Leuven Tel: 32 16 281 301 Fax: 32 16 281 501
B2: Materials for a Ferroelectric Capacitor Stack with direct contact to silicon	Dr.ir. Dirk Wouters IMEC, Division MAP-ARS Kapeldreef 75 B-3001 Leuven Tel: 32 16 281 301 Fax: 32 16 281 501
B3: Materials for a ferroelectric Capacitor Stack with direct contact to silicon	Dr. Smeets Jozef VITO, Materials Division Boeretang 200 B-2400 Mol Tel: 32 14 333 184 Fax: 32 14 321 186

CH1: Reliability of ferroelectric thin films	Prof. N. Setter MX-LC Ecublens CH-1015 Lausanne Tel: 41 21 693 29 61/75 Fax: 41 21 693 29 35
CH2: Novel polarised ferroelectric thin films for silicon integrated devices	Prof. Francis Lévy IPA-EPFL, Dept. de Physique CH-1015 Lausanne Tel: 41 21 693 11 11 Fax: 41 21 693 46 66

D1: Charge transport, dc field effects, and long-term reliability of electroceramic thin films	Dipl.Ing. Guido Dietz Institut für Werkstoffe der Elektrotechnik II RWTH Aachen Univ. of Technology D-52056 Aachen Tel: 49 241 80 7812 Fax: 49 241 87 6389

DK1: Ferroelectric Thin Films for Saw Devices	Dr. C. Millar Ferroperm Ltd., Piezceramics Div. Hejreskovvej 6 DK-3490 Kvistgard Tel: 45 49 13 82 90 Fax: 45 49 13 81 88

E1: Ferroelectric Thin Films for Saw Devices	Prof. J. Mendiola Dpto. de Materiales Ferroeléctr. ICMM-A. CSIC. Serrano 144 E-28006 Madrid Tel: 34 1 561 88 06 Fax: 34 1 411 76 51

I1: Materials for a ferroelectric capacitor stack with direct contact to silicon	Dr. Bernard Enrico Watts Instituto MASPEC/CNR Via Chiavari 18a I-43100 Parma Tel: 39 521 269 207 Fax: 39 521 269 206
I2: Materials for a ferroelectric capacitor stack with direct contact to silicon	Prof. Maria Allegrini Dipartimento di Fisica, Univ. di Pisa Piazza Toricelli 2 I-56100 Pisa Tel: 39 50 911 282 Fax: 39 50 482 77

S1: Pulsed Laser Ablation Deposition of Ferroelectric Thin Films	Prof. K. V. Rao Royal Institute of Technology Dept. of Condensed Matter Physics Valhallavägen S-100 44 Stockholm Tel: 46 8 790 77 71 Fax: 46 8 790 77 71

S2: Ferroelectric Thin Films	Prof. Richard Warren Dr. True Lindbäck LuTH, Div. of Engineering Materials SE-951 87 Lulea Tel: ++ 46-929-910 00 Fax: ++ 46-920-972 88

SF1: Pulsed laser ablation deposition of ferroelectric thin films	Prof. Seppo Leppävuori University of Oulu, Dept. of Electrical Engineering Linnanmaa SF-90570 Oulo Tel: 358 81 553 27 11 Fax: 358 81 553 27 28

SLO1: Sol-gel processing of thin films with ferroelectric or conducting properties	Dr. Marija Kosec "Jozef Stefan" Institute, Univ. of Ljubljana Jamova 39 SLO-61000 Ljubljana Tel: 386 61 125 91 99 Fax: 386 61 219 385 273 677

TUR1: Ferroelectric Ceramic Thin Films	Prof. Dr. A.M. Özenbas Dept. of Metallurgical Eng. TR-METU - 06531 Ankara Tel: + 90-312-210 10 00/2532 Fax: + 90-312-210 12 67

UK1: Pulsed laser ablation deposition of ferroelectric thin films	Dr. Ian W. Boyd Dept. of Electronic and Electrical Engineering, Univ. College London Torrington Place UK-London WC1E 7JE Tel: 44 71 387 7050 ex 3956 Fax: 44 71 387 4350
UK2: Pulsed laser ablation deposition of ferroelectric thin films	Dr. Arthur E. Hill Dept. of Electronic and Electrical Engineering, Univ. of Salford UK-SALFORD M5 4WT Tel: 44 61 745 5000 ex 4761 Fax: 44 61 745 5999
UK3: Ferroelectric Ceramic Thin Films for Saw Devices	Dr. D.A. Hall Materials Science Centre University of Manchester Grosvenor Street UK-Manchester M1 7HS Tel: 44 61 200 3577 Fax: 44 61 200 3586

UK4: Reliability of Ferroelectric Thin Films	Dr. W. Lee Dr. I.M. Reaney Dept. of Engineering Mater. University of Sheffield Sir Robert Hadfield Building Mappin Street GB-Sheffield, S1 4DU Tel: + 44-742-82 54 74 Fax: + 44-742-75 43 25

MANAGEMENT COMMITTEE MEMBERS COST 514

B- **Dr. J. Smeets**
VITO
Materials Division
Boeretang 200
B- 2400 Mol

Tel. 32 14 335634
Fax 32 14 321186
E-m. smeetsj@vito.be

B- **Dr. D. Wouters**
Interuniversity
Micro-Electronics Center (IMEC)
Kapeldreef 75
B- 3001 Leuven

Tel. 32 16 281301
Fax 32 16 281501
E-m. wouters@imec.be

CH- **Prof. Nava Setter (Ms)**
Ecole Polytechnique Fédérale de Lausanne
Lab. de céramique
MX-D Ecublens
CH- 1015 Lausanne

Tel. 41 21 6932961
Fax 41 21 6935810
E-m. nava.setter@ lc.dmx.epfl.ch

CZ- **Dr. J. Petzelt**
Institute Physics ASCR
Na Slovance 2
CZ- 18040 PRAHA 8 - Liben

Tel. 420 2 66052166
Fax 420 2 821227
E-m. petzelt@fzu.cz

D- **Prof. Dr. Ing. Rainer Waser**
Inst. für Werksstoffe der Elektrotechnik RWTH
D- 52056 Aachen

Tel. 49 241 807813
Fax 49 241 8888300
E-m.

DK- **Dr. Wanda W. Wolny (Ms)**
Ferroperm A/S
Hejreskovvej 6
DK- 3490 Kvistgard

Tel. 45 49 138190
Fax 45 49 138188
E-m.

E- **Dr. P. Duran**
Electroceramic Dept.
Instituto de Ceramica y vidrio
Crta de Valencia - K 23.4
E- 28500 Arganda del Rey

Tel. 34 1 8711800
Fax 34 1 8700550
E-m.

E- **Dra. Lorena Pardo (Ms) Chairperson**
Inst. de Ciencia de Materiales
CSIC
Cantoblanco
E- 28049 Madrid

Tel. 34 1 3349066
Fax 34 1 3720623
E-m. immlp73@cc.csic.es

F- **Dr. Robert Farhi** - Directeur du LPMC
Université de Picardie Jules Verne
Faculté des Sciences
33 rue Saint-Leu
F- 80039 Amiens Cedex

Tel. 33 3 22827618
Fax 33 3 22827891
E-m. robert.Farhi@sc.u-picardie.fr

F- **M. Snoeck**
CEMES
LOE/CNRS
29 rue Jeanne Marvig - BP 4349
F- 31055 Toulouse Cedex

Tel. 33 5 62257891
Fax 33 562257999
E-m.

FIN- **Prof. Seppo Leppävuori**
University of OULU
Micorelectronics and Material Physics Laboratories
FIN- 90570 OULU

Tel. 358 85532711
Fax 358 85532728
E-m.

I- **Prof. Fabrizio Leccabue**
Instituto Maspec CNR
Via Chiavari, 18 a
I- 43100 Parma

Tel. 39 521 269207
Fax 39 521 269206
E-m. Leccabue@ prmasp.maspec.bo.cnr.it

I- **Dr. Bernard Watts**
Instituto Maspec CNR
Via Chiavari, 18 a
I- 43100 Parma

Tel. 39 521 269207
Fax 39 521 269206
E-m. Leccabue@ prmasp.maspec.bo.cnr.it

IRL- **Dr. Gabriel Crean**
NMRC
Lee Maltings
Prospect Row
IRL- Cork

Tel. 353 21 904321
Fax 353 21 270271
E-m. gcrean@nmrc.ucc.ie

LV- **Dr. Andris Sternberg**
University of Latvia
Institute of Solid State Physics
Ferroelectric Physics Department
8 Kengaraga St.
LV- 1063 Riga

Tel. 371 2 261304
Fax 371 7112583
E-m. stern@acad.latnet.lv

P- **Dr. M.J.M. GOMES**
Universidad da Minho
Dep. Fisica
P- BRAGA

Tel. 351 53 604327/0
Fax 351 53 67 89 81
E-m. mjesus@fisica.uminho.pt

S- **Prof. K.V. Rao**
Royal Institut of Technology
Dept of Condensed Material Physics
S- 100444 Stockholm

Tel. 46 8 7907771
Fax 46 8 7907771
E-m. rao@emp.kth.se

SLO- **Dr. Marija Kosec (Ms)**
Josef Stefan Institute
Jamova 39
SLO- 1000 Ljubljana

Tel. 386 61 1773900
Fax 386 61 1263126 or 386 61 219385
E-m. marija.kosec@ijs.si

TR- **Prof. Macit Ôzenbas**
SEKOM Middle East Technical University
Dept. Metallurgical Engineering
TR- 06531 Ankara

Tel. 90 312 2102532
Fax 90 312 2101267
E-m. ozenbas@rorqual.cc.metu.edu.tr

UK- **Dr. David Hall**
University of Manchester & UMIST
Materials Science Centre
Grosvenor Street
UK- M1 7HS Manchester

Tel. 44 161 200 3577
Fax 44 161 200 3586
E-m. David.hall@man.ac.uk

E.C. **Dr. Peter LOBOTKA**
European Commission, DG XII/B1
200 rue de la Loi, SDME 1/44
B-1049 Brussels

Tel. 32 2 296 55 12
Fax 32 2 296 59 25
E-m. p.lobotka@dg12.cec.be

Deputies :

SLO- **Dr. Barbara Malic**
Josef Stefan Institute
Jamova 39
SLO- 1000 Ljubljana

Tel.
Fax
E-m. barbara.malic@ijs.si

Workshop of the

COST 514
European Concerted Action on Ferroelectric Thin Films

ICMM.CSIC.
Madrid (SPAIN)
4-5 March 1996

The COST514 Action of the EU on Ferroelectric Thin Films started in 1993 as an effort to coordinate on an European level the scientific research on the topic funded nationally. It promotes the realization of Short Term Scientific Missions, for a maximum period of one month, among the researchers working in the laboratories of the countries joined to the Action. It also sponsor an annual Workshop to present the activities of these laboratories. A start-up workshop was organized by Prof. K.V. Rao of the Swedish Royal Institute in Stockholm on 6-7 May 1994. The 1995 Workshop was organized at the "Ecole Polytechnique Fédérale de Lausanne" (EPFL) (Switzerland) by the chairwoman of the Action Prof. N. Setter on 16-17 February 1995.

As decided in the Management Committe Meeting of the COST514 EU Action that took place in Nijmegen (The Netherlands) on 5 July 1995, the 1996 Workshop has taken place in the "Instituto de Ciencia de Materiales (C.S.I.C.)" in its new location at Cantoblanco, Madrid (Spain), on 4-5 March 1996.

We would like to thank all the attendants for their interesting contributions - here collected - discussions and new ideas, and to all the staff and students of the "Departamento de Materiales Ferroeléctricos" of this Institute:

Prof. Jesús Mendiola
Prof. Basilio Jiménez
Dr. Carlos Zaldo
Dr. Carlos Alemany
Dr. Francisco Carmona
Dr. Enrique Maurer
Luis Contreras
Francisco Díaz
Rafael Sirera
Pablo Ramos
Miguel Algueró
María José Martín
Pedro Durán-Martín
Carmen Coya
Edgar Alfonso
José María Vega

for their scientific and technical assistance for the development of the Workshop.

Madrid, March 1996.

Dra. María Lourdes Calzada
Dra. Lorena Pardo.
1996 COST514 Workshop Organizers.

COST 514 EU ACTION WORKSHOP
"FERROELECTRIC THIN FILMS"

Departamento de Materiales Ferroeléctricos.
Instituto de Ciencia de Materiales de Madrid (ICMM). C.S.I.C.
Cantoblanco. 28049 - Madrid (SPAIN) 4-5 March, 1996

PROGRAM

Monday 4th March

09:30 **Arrival** and collect of documentation.

09:45 **Introductory remarks** by Dr. M. Kosec (by Prof. Nava Setter, Chairwoman of the COST514 Action) and Local Organizers.

SESSION I: Chairwomans: Dr. M. Kosec and L. Pardo.

09:50 - 10:35 Invited talk 1: "**Survey of Developments in Ferroelectric Nonvolatile memories in the USA and Japan**".
Prof. Angus I. Kingon. North Carolina University (U.S.A.)

10:35 - 10:55 Contributed talk 1: "**Ferroelectric characterization of sol-gel modified PbTiO3 Ferroelectric Thin Films**"
Prof. J. Mendiola. ICMM (Spain)

11:00 - 11:30 Coffe Break.

SESSION II: Chairwoman: Dr. M.L. Calzada.

11:30 - 12:15 IT2: "**Ferroelectric Thin Films: Important Applications and Required Material Improvements**"
Dr. W. Wersing. Siemens AG (Germany)

12:15 - 12:35 CT2: "**TEM Studies on Sol-Gel Processed Modified Lead Titanate Thin Films**".
Dr. Etienne Snoeck. CEMES-LOE (France)

12:35 - 12:55 CT3: "**Piezoelectric Measurements and Piezoelectric Fatigue on PZT Thin Films**".
Dr. Andrei Holkin. EPFL (Switzerland)

13:00 - 14:00 Lunch.

SESSION III: Chairman: Prof. S. Lepävuori.

14:00 - 14:30 IT3: "**Measurements of Ferroelectric and Electrostrictive Properties on Lead Titanate Based and PLZT Thin Films** ".
Prof. A. Sternberg. University of Latvia at Riga (Latvia)

14:30 - 14:50 CT4: "**Current Studies on Ferroelectric Thin Films in Stockholm**".
Prof. K.V. Rao. Royal Institute of Technology (Sweden)

14:50 - 15:10 CT5: "**Electrical Properties of Lithium Tantalate Thin Films on Silicon Substrates**"
Drs. Charles-Henry Kohli, P.E. Schmid and F. Levy . EPFL (Switzerland)

15:10 - 15:30 CT6: "**Thermal Annealing of Pt Sputtering and RIE Induced Defects in PZT Ferroelectric Capacitors**"
Dr. Dirk Wouters. IMEC (Belgium)

15:30 - 16:00 Pause

Monday 4th March (cont.)

SESSION IV: Chairman: Dr. W. Wersing.
16:00 - 16:30 CT7: **"Processing Parameters affecting the Properties of Sol-Gel derived Modified Lead Titanate Thin Films"**
Dr. M. Lourdes Calzada. ICMM (Madrid)
16:30 - 16:50 CT8: **"Precursor Chemistry and Properties of Sol-Gel PZT Thin Films"**
Dr. Marija Kosec. Josef Stefan Institute (Slovenia)
16:50 - 17:10 CT9: **"Preparation of PZT Films and Powders by the Sol-Gel Process"**
Prof. A. Macit Özenbaş. Middle East Technical University (TurKey)
17:10 -17:30 CT10: **"Barium Titanate Thin Films: Influence of Precursor Chemistry and Processing on Thin Film Properties"**
Dipl.Phys. S. Hoffmann and Prof. R. Waser. RWTH Aachen (Germany)

Tuesday 5th March.

SESSION V: Chairman: Prof. I. Boyd.
09:30 - 10:15 IT4: **"Laser ablation deposited ferroelectric thin films"**
Prof. A. Safari. Rutgers University (U.S.A.)
10:15 - 10:35 CT11: **"Pulsed laser deposition and electrical characterization of Ca-modified lead titanate thin films"**
Dr. C. Zaldo. ICMM (Spain)
10:35 - 10:55 CT12: **"Factors Controlling the Phase Distribution of PZT Thin Films Prepared by PLD"**
Drs. B.E.Watts and F. Leccabue. MASPEC CNR (Italy)
10:55 - 11:15 Coffe Break.

11:15 - 11:30 **Project Meetings** for the Preparation of yearly report and 15 minutes presentation for each project.

SESSION VI: Chairwoman : Dr. L. Pardo.
11:30 - 12:20 **Presentation** for each project leader:
1.- Reliability of Ferroelectric Thin Films (Dr. M. Kosec)
2.- Materials for a Ferroelectric Capacitor Stack in direct contact to Silicon (Dr. D. Wouters)
3.- Optical and Non-linear Optical properties of Ceramic Thin Films (Dr. B.E. Watts)
4.- Pulsed Laser Ablation Deposition of Ferroelectric Thin Films (Prof. K.V. Rao)
5.- Ferroelectric Thin Films for SAW devices (Dr. L. Pardo)
12:20 - 13:00 **Open Discussion of the State of the Art on Ferroelectric Thin Films.**
Farewell to the participants.
13:00 - 14:00 Lunch.

14:30 - 15:30 **Visit to Laboratories.**

COST 514 EU ACTION WORKSHOP
"FERROELECTRIC THIN FILMS"

LIST OF PARTICIPANTS

Dr. A.Macit Özenbas
Dept. of Metallurgical Eng.
Middle East Technical University
06531 Ankara
TURKEY
Tel: 90 312-2101000/2532
Fax: 90 312-2101267
E-mail: ozenbas@rorqual.cc.metu.edu.tr

Dr.Bernard Enrico Watts
Instituto MASPEC/CNR
Via Chiavari 18A
I-43100 Parma
ITALY
Tel: 39 521 269207
Fax: 39 521 269206

Prof. Fabrizio Leccabue
Instituto Materiali Speciali per Elettronica e Magnetismo
Consiglio Nazionale delle Ricerche
Via Chiavari 18/A
43100 Parma
ITALY
Tel: 39 521 2691
Fax: 39 521269206
E-mail: leccabue@prmasp.bo.cnr.it

Prof. Pedro Mantas
Universidade de Aveiro
Depto. Engenharia Cerâmica e do Vidro
Campo Universitário
3800 Aveiro
PORTUGAL
Tel: 351-34-370200
Fax: 351-34-25300

Dr. Charles-Henry Kohli
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Institut de Physique Appliquée
Département de Physique
CH-1015 Lausanne
SWITZERLAND
Tel: 41-21-693 44 36
Fax: 41-21-693 46 66
E-mail: kholi@ipasg.epfl.ch

Dr. Enrico Colla (by Prof. Nava Setter)
Dr. Andrei Kholkin
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Laboratoire de Céramique.
MX - C Ecublens
CH- 1015 Lausanne
SWITZERLAND
Tel: 41-21- 693 29 61
Fax: 41-21- 693 58 10.

Dr.Ing. Dirk Wouters
IMEC, Division MAP-ARS
Kapeldreef 75
B-3001 Leuvcen
BELGIUM
Tel: 23-16-281301
Fax: 32-16-281501
E-mail: wouters@imec.be

Prof. Ian W.Boyd
Dept. of Electronic and Electrical Eng.
University College London
Torrington Place
London WC1E 7JE
UNITED KINGDOM
Tel: 44 171 380 73 00/2
Fax: 44 171388 93 25
E-mail: i.boyd@eleceng.ucl.ac.uk

Dr. D.A.Hall
Materials Science Centre
University of Manchester
Grosvenor St.
Manchester M1 7HS
UNITED KINGDOM
Tel: 44-161-2003577
Fax: 44-161-20035 86

Prof. K.V.Rao
Royal Institute of Technology
Dept. of Condensed Matter Physics
Valhallavägen
S-100 44 Stockholm
SWEDEN
Tel: 46-8 7907771
Fax: 46-8 7907771
E-mail: rao@cmp.jth.se

Prof. Seppo Leppävuori
Microelectronics and Material Physics
Laboratories
Dept. of Electrical Engineering
University of Oulu
Linnanmaa
FIN-90570 OULU
FINLAND
Tel: 358 81 5532710
Fax: 358 81 5532728
E-mail: sele@ee.oulu.fi

Dr. Etienne Snoeck
CEMES-LOE/CNRS
29, rue Jeanne Marvig, BP 4349
31055 Toulouse Cedex
FRANCE
Tel: 33-62-257891
Fax: 33-62-257999
E-mail: snoeck@cemes.fr

Ms. Wanda W. Wolny
Dr. Andrew James
Industriselskabet Ferroperm A/S
Piezoelectric Ceramics Division
Hejeskovvej 6
3490 Kvistgård
DENMARK
Tel: 45-49-138290
Fax: 45-49-138188
E-mail: ferrop@inet.uni-c.dk

Dr. Marija Kosec
"Jozef Stefan" Institute
Jamova 39
61111 Ljubljana
SLOVENIA
Tel: 386-61-17 73 900
Fax: 386-61-126 3 126

Dipl. Phys. S. Hoffman
Institut für Werkstoffe der Elektrotechnik II
Lehrstuhl II
RWTH Aachen
Sommerfeldstr., 24
D-52074 Aachen
GERMANY
Tel: 49-241-80 78 22
Fax: 49-241-88 88 300

Prof. Pedro Durán
Prof. Carlos Moure
Inst. de Cerámica y Vidrio (C.S.I.C.)
Antigüa Carretera de Valencia, km 24,300
28500 - Arganda del Rey
Madrid
SPAIN
Tel: 34-1-8711800/04
Fax: 34-1-870 05 50

Prof. Jesús Mendiola.
Dra. Maria Lourdes Calzada
Dr. Carlos Zaldo
Dra. Lorena Pardo
Instituto de Ciencia de Materiales
de Madrid. C.S.I.C.
Cantoblanco
28049 - Madrid
SPAIN
Tel: 34 -1-334 90 00
Fax: 34-1-372 06 23

Prof. Angus I.Kingon
North Carolina State University
Materials Research Center
Dept. of Materials Science and Engineering
P.O. BOX 7907
Raleigh, N.C. 27695-7907
USA
Tel: 1 -919-515 8636
Fax: 1 -919-515 3419
E-mail: kingon@mat.mte.ncsu.edu

Prof. A.Safari
Dept. of Ceramic Engineering and Center
for Ceramic Research
Rutgers, The State University of New Jersey
Brett and Bowser Roads, P.O.Box 909
Piscataway, NJ 08855-0909
USA
Tel: 1- 908- 445 4367
Fax: 1 -908-445 5577
E-mail: safari@safari.rutgers.ed

Dr. Andris Sternberg
Institute of Solid State Physics
University of Latvia
8 Kengaraga Str.
LV1063 Riga
LATVIA
Tel: 371-2-261 304
Fax: 371-2-260 543
E-mail: stern@acad.latnet.lv

Dr. W.Wersing
SIEMENS AG
Corporate Research and Development
ZFE BT MR 2
Otto-Hahn-Ring 6
81739 München 83
GERMANY
Tel: 49-89-636-52680
Fax: 49-89 63648131
E-mail: wolfram.wersing@zfe.siemens.de

Dr. Martin Kedro
COST 514 Officer
European Commission
General Directorate for Science, Research
and Development
Joint Research Centre
DG XII B/1
200, rue de la Loi -B-1049 Bruxelles
BELGIUM
Tel: 32-2-296-55 12
Fax: 32-2-296 59 25

Invited Talks

“Survey of Developments in Ferroelectric Nonvolatile Memories in the USA and Japan”

Prof. A.I. Kingon. North Carolina University (U.S.A.).

IT2

"Ferroelectric Thin Films:Important Applications and Required Material Improvements"

Dr. W. Wersing. Siemens AG (Germany).

MEASUREMENTS OF FERROELECTRIC AND ELECTROSTRICTIVE PROPERTIES ON LEAD CONTAINING PEROVSKITE THIN FILMS

A.Sternberg, M.Tyunina, M.Kundzinsh, V.Zauls, M.Ozolinsh, E.Birks, L.Shebanovs, L.Calzada[1], L.Pardo[1], M.Kosec[2], K.V.Rao[3], R.Kullmer[4]
Institute of Solid State Physics (ISSP), University of Latvia, Riga, Latvia;
[1] *Instituto de Ciencia de Materiales de Madrid, C.I.S.C., Spain;*
[2] *Jozef Stefan Institute (JSI), Ljubljana, Slovenia;*
[3] *Royal Institute of Technology (RIT), Stockholm, Sweden;*
[4] *Johannes Kepler University (JKU), Austria*

INTRODUCTION

The physical background of diffused phase transitions (PT) (in relaxors) as well as field-induced first-order ferroelectric-paraelectric, antiferroelectric-ferroelectric phase transitions in modified perovskite compositions has been studied at the Institute of Solid State Physics of the University of Latvia during a 20-year experience of synthesis, investigation, and application of lead containing perovskites, mainly in the form of bulk ceramics. A number of diverse physical effects important to the efficiency of any particular application have been analyzed with respect to the nature of PT and state of polarization. Efficient electrooptic PLZT and PSN based ceramics, pyroelectric and electrocaloric PST compounds have been of special concern with regard to a number of applications. The recent technological trends of introducing thin film ferroelectrics (nonvolatile memories, pyroelectric detectors, micromechanical sensors and actuators) have challenged to find, how the ferroelectric and related properties of developed bulk ceramic compounds are maintained in thin film products of the same composition. With COPERNICUS project and technological cooperation with the Royal Institute of Technology (Stockholm) and Johannes Kepler University (Linz) we have started with studies of PLZT, PSN and PST heterostructures.

1. THIN FILM PRODUCTION

1.1. Pulsed laser deposition (PLD)

PLD parameters were experimentally optimized with respect to ferroelectric (FE) and dielectric (DE) properties of the PLZT, PZT, PSN and PST thin films the single crystal $LaAlO_3$ and MgO substrates with YBCO bottom electrode being used (Fig.1). As targets for PLD dense pellets of ceramics produced in the ISSP were used.

Two different laser facilities were examined: Nd:YAG laser (355 nm), duration 10 ns, repetition rate 10 Hz, and excimer KrF laser (248 nm), pulse duration 30 ns, repetition rate 5 Hz. Target- substrate distance was fixed in the range 40 to 55 mm. Substrates were heated to 550^0C, since further increase of deposition temperature could result in lead deficient films. Post-annealing temperature was equal to 400^0C and cooling rate did not exceed 10^0C/min. The laser fluence and ambient oxygen pressure were optimized with respect to FE/DE parameters of the films with thickness 0,5 μm.

Experiments have shown that the largest values of dielectric permittivity and polarization were characteristic for films deposited at E=3,0 J/cm^2, 200 mTorr oxygen (Nd:YAG laser) and E=2,0 J/cm^2, 300 mTorr oxygen (KrF laser).

The studies of the film surface morphology have shown submicron and micron size particles including both droplets from the targets and various types of outgrowths in YBCO layer. The films consisted of grains of 20 to 1000 nm in diameter, depending on deposition conditions. Films demonstrating the best dielectric and ferroelectric properties contained 100-200 nm grains.

X-ray analysis of the produced heterostructures has revealed epitaxial growth of [100] oriented perovskite PLZT films on MgO/YBCO substrate.

The main characteristics of the films deposited under optimum conditions are summarized in Table 1.

1.2. Sol-gel processing

Calcium modified lead titanate $Pb_{0.76}Ca_{0.24}TiO_3$ films are obtained by sol-gel processing. Sol-gel as alternative technology was used for preparation of PLZT films at Jozef Stefan Institute. Precursors - Pb acetate trihydrate, La acetate hydrate, Ti and Zr n-propoxides were selected. PLZT solutions were deposited by spin coating technique on $Pt/Ti/SiO_2/Si$ substrates and fired for 20 hours at 600°C. To minimize pyrochlore phase a $PbTiO_3$ layer was used to deposit the PLZT on.

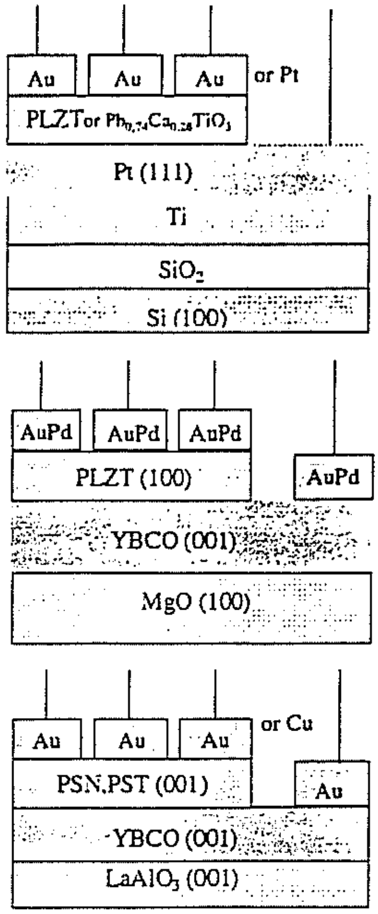

Figure 1. Schematic cross-section of the produced heterostructures.

2. FERROELECTRIC AND DIELECTRIC CHARACTERISTICS

Dielectric measurements (HP 4284 LCR, -100 - +400°C, 20 - 10^6 Hz) show a dependence on composition and are strongly affected by the electrode material and contact quality, as well as by the homogeneity and thickness of the film. Typical thin film characteristics are represented in Fig.2 (P-E measurements) and Fig.3 (ε-T curves).

Table 1

Dielectric characteristics of thin films with respect to bulk ceramic material; ε and tgδ measured at 10 kHz; remanent polarization P_r, full polarization P_f and coercive field E_c obtained from hysteresis loops at 150 Hz. T=20°C.

Compositions	Technology	ε,	tgδ,	P_r, μC/cm²	P_f, μC/cm²	E_c, kV/cm²
PLZT 6/65/35	film (PLD)	250-350	0.02-0.05	6-8	25-30	40-60
PLZT 9.75/65/35	film (PLD)	150-250	0.05-0.15	4-5	15-20	40-60
PLZT 9.5/65/35	film (sol-gel)	600-800	0.05-0.15	5-7	25-30	25-50
PLZT 8/65/35	*bulk*	*2000*	*0.03*	*21*	*25*	*4*
PLZT 9.5/65/35	*bulk*	*4000*	*0.03*	*0*	*12*	*0*
PZT 65/35	film (PLD)	800	0.05-0.15	30	40	40
PZT 65/35	*bulk*	*1000*	*0.03*	*31*	*40*	*9*
PST	film (PLD)	300-450	0.03-0.05	4	15-17	40-60
PST	*bulk*	*4000-6000*	*0.02-0.03*	*0*	*10*	*0*
PSN	film (PLD)	250-300	0.05-0.2	3	13-15	25
PSN	*bulk*	*150-200*	*0.02-0.03*	*20-25*	*25-30*	*4-5*

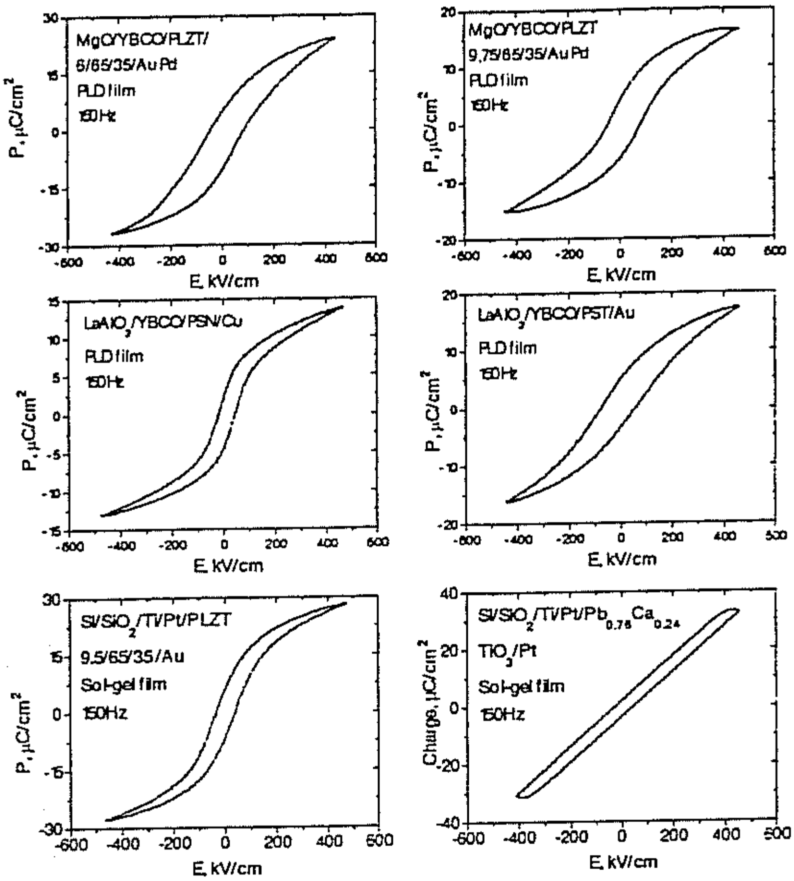

Figure 2. Dielectric hysteresis loops of thin films.

A strong frequency dependence in the range 50 kHz-1 MHz is observed, e.g., in PLZT films on MgO/YBCO substrate obtained by PLD (Fig.4) - ε decreases with increasing frequency, while tgδ increases at the same time. It resembles Debye relaxation. In heterostructures it is rather possible that capacity (FE thin film) is in series with resistivity (electrode). On its turn, the resistivity of the FE film itself can be approximated by the equivalent circuit parallel to the capacity being measured. In some samples, where it is <1MΩ, it may provide an undesired leakage and charge accumulation at measuring the hysteresis, in which case the obtained parameters cannot be interpreted as polarization, see, e.g., the hysteresis of one of sample capacitors in PTCA film (Fig.2).

Typical DE and FE characteristics of the films with respect to bulk material are demonstrated in Table 1. Thus, PLZT compositions, obtained both by PLD or sol-gel route show satisfactory ferroelectric properties; films formed by PLD possess a better and uniform over the film resistivity(>100MΩ).

Usually E_c and tgδ are larger and ε - smaller compared to PLZT bulk material. There is no large difference in E_c values in LPD obtained PLZT 6/65/35 and PLZT 9.75/65/35 films; it seems that slim loop ferroelectrics (like bulk PLZT 9.75/65/35) is hard to achieve in thin film condition. However, the sol-gel derived PLZT 9.5/65/35 show hysteresis loop with lower E_c being more similar to those of bulk composition (Fig.2).

The PLD films of PSN exhibit more rectangular hysteresis than PLZT. However, the polarization values are considerably less as compared to ceramics or PLZT films oriented along a-axis. One of the reasons might be the strongly pronounced c-axis orientation of PSN films, i.e., the structural elements subject to switching are oriented along the measuring field and the gain from switching is minimized. The ε-T is essentially more diffused as compared with ceramic material and is observed at ~150°C (Fig.3) being about 50° higher compared to that in disordered PSN ceramics. As to the PST film (highly c-axis oriented, too) ε is remarkably smaller than in ceramics. The ε-T curve essentially broadens and shifts to -30°C (Fig.3).

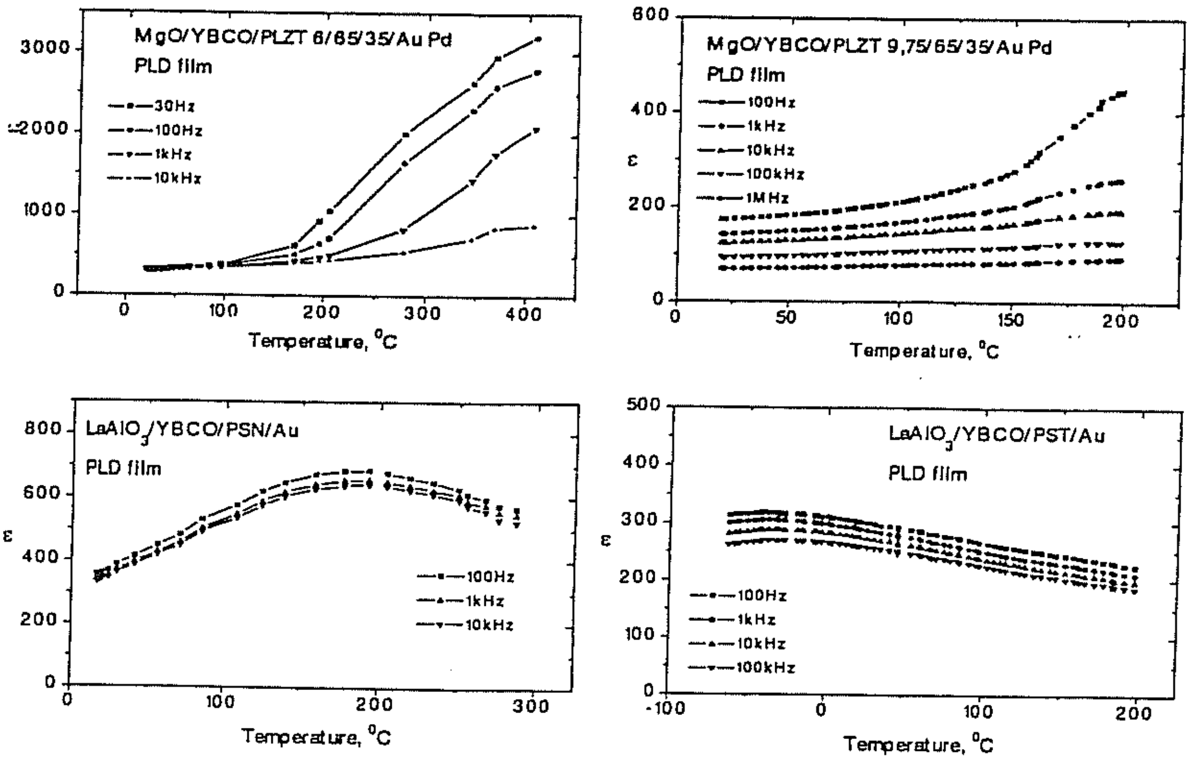

Figure 3. Temperature dependence of dielectric permittivity of thin films.

Although there are no data on B-site cation ordering in both PSN and PST films obtained, one may propose the material being disordered. The opposite shifts of the dielectric permittivity maximum are characteristic in disordered bulk materials: to higher temperatures in case of PSN, and to lower temperatures in case of PST. The change of hysteresis loops of PST film with the temperature is definitely monotonous in a wide range. No maximum of ε(T) has been observed in PLZT films. A weak dispersion of thermal dependence of ε (Fig.3) and tgδ is observed in PLD film of PLZT 9.75/65/35.

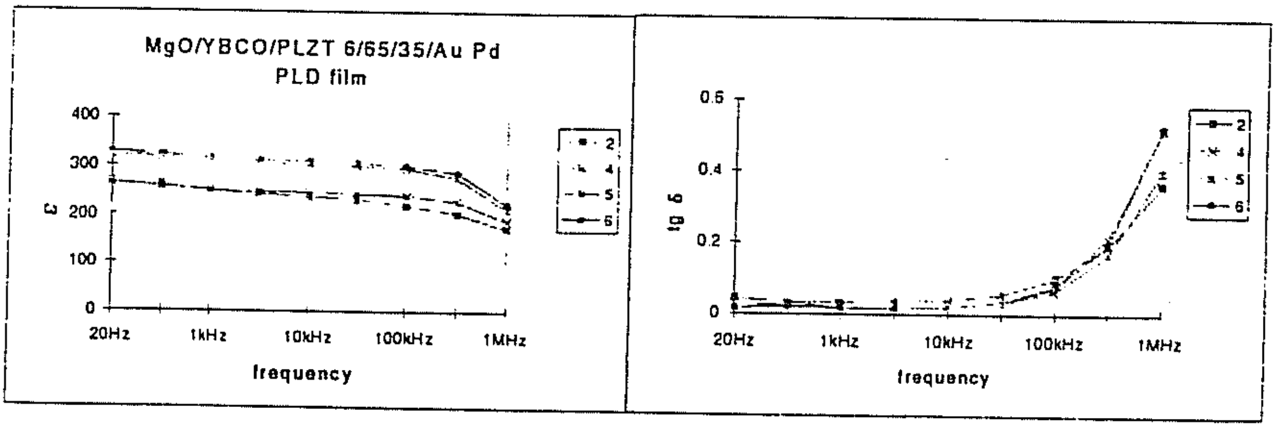

Figure 4. Frequency dependence of ε and tgδ of PLZT 6/65/35 thin film.

3. DEFORMATION OF PSN THIN FILM

The experimental set-up of modified Michelson interferometer is shown on Fig.5. The AC modulation techniques is used to increase sensitivity.

Reference phase φ modulation was achieved by piezo driven mirror, the DC voltage and lock-in output being recorded by a computer. To analyze small samples the arm of interferometer is equipped with microscope lens. Direct reflection from the metal top electrode is used.

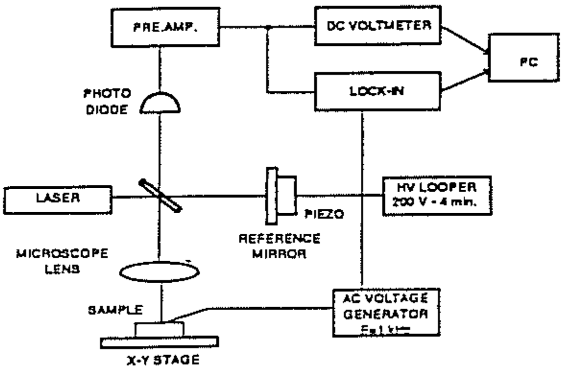

Figure 5. Experimental set-up of interferometric technique for small displacement measurements.

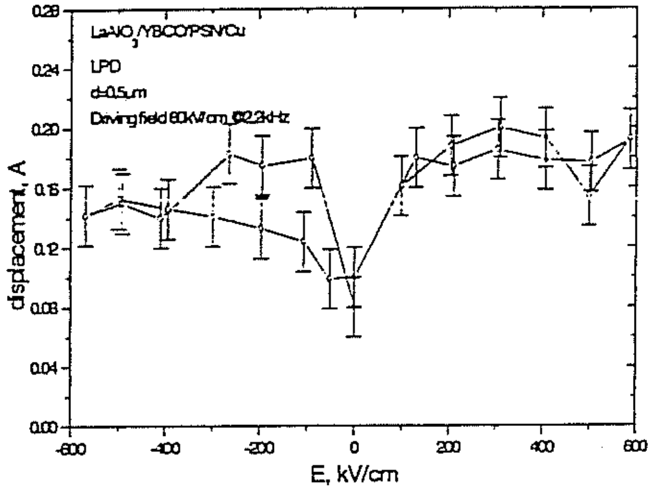

Figure 6. Strain hysteresis in PSN thin film. Driving field 60 kV/cm; frequency 2.2 Hz.

The AC driving voltage-induced sample surface oscillations result in appearance of a small AC signal component in the interference light intensity measured by a photodetector. The lock-in amplifier detects this small AC signal component the length of the reference arm being adjusted by a mirror mounted on piezo-transducer to achieve maximum lock-in readout. It is possible to stabilize interferometer at this so called π/2 phase difference point by means of electronic feedback system. The estimated sensitivity limit is of the order of 10^{-2} Å. Reliable reflections from the electrodes is the main problem; thin poorly reflecting electrodes are not suitable.

Displacements of 0.6 Å for driving voltage 30 V at 1 kHz were recorded with laser deposited YBCO / PST / Cu samples (thickness ~0.5 μm). Displacement measurements with DC bias from -30 to +30 the AC driving voltage being maintained at 3V rms. show signal saturation at 5V bias (Fig.6). Relatively small strain values obtained may be partly attributed to c-axis oriented structure of the measured PST film. Laser interferometric measurements are in progress.

4. FATIGUE TEST OF THIN FILMS

A modified Sawyer-Tower circuit and bipolar pulses were used to evaluate fatigue. The rise time of the pulses was $\tau = 2.5 \times 10^{-7}$ s for sample capacitance $C_x = 5$ nF. The polarization pulse response of the sample - the amplitude of the AC signal on the reference capacitance was detected, the polarization P(t) of the sample being simultaneously measured by the digital oscilloscope. The charge of polarization reversal vs. voltage diagram (Fig.7) shows the decrease of reversible polarization (charge) with the number of polarization switching cycles. For "small" values of the pulse voltage 5-10 V (100-200 kV/cm) samples with at least satisfactory electrodes during the life tests reveal no diminishing of dielectric properties. The increase of the test pulse voltage (and sequentially the increase of the recharge current) leads to the effective decrease of the polarization response by increasing the number of cycles.

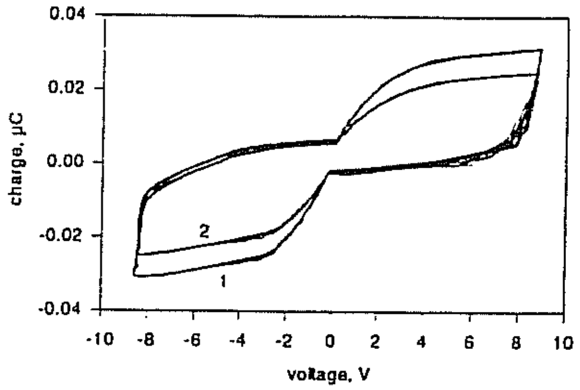

Figure 7. Charge (polarization) vs. voltage phase diagram of PLZT 9.75/65/35 sample before (1) and after (2) the life test (pulse amplitude 30 V, period 10 μs, number of cycles 2x10^{9}.

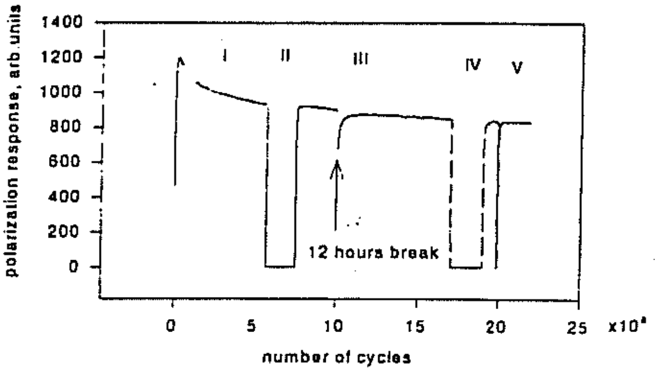

Figure 8. Life test of laser pulsed deposited PLZT 9.75/65/35 amplitude of bipolar pulses 30 V (steps I, III, V) and 0 V (steps II and IV) pulse length 2.5 μs and period 10 μs.

The decrease of the effective capacitance depends on conditions of the test, and, on average, lays within the limits of 20-30% and more during 10^{9} cycles for pulse amplitude 20 V and higher. The following are observed: (1) the greater is the test pulse voltage and/or capacitance of the sample, the greater is the destroying rate; (2) in the case when the upper (sputtered) electrode is additionally covered with a layer of silver paint one can obviously observe that an effective destroying of such sample as a capacitor begins at a higher pulse voltage as compared with the case of sputtered electrode only.

It is interesting, that (observed not for all samples studied) applying of bipolar pulses (the pulse number up to 10^{8} after a longer still-stand up to 12 hours) sometimes leads to some "recovering" of the polarization reversal - the pulse polarization response is increasing during this stage of the life test (see Fig. 8). The nature of this effect is still not clear - the increase of the measured effective value of the charge on the reference capacitor C_o can be a result of internal heating of the sample, due to some diminishing of the sample leakage resistance, as well as to more complicated processes increasing the pulse response of thin film dielectric layer.

CONCLUSIONS

Results of thin film technology optimization experiments suggest that properties like dielectric dispersion, polarization switching characteristics, fatigue are essentially affected by the heterostructure.

The PLD thin PLZT films (a-axis oriented), the pulsed laser deposited PSN and PST films (c-axis oriented) and sol-gel derived PLZT films (randomly oriented) show satisfactory ferroelectric properties. PLZT films formed by PLD possess a better and uniform over the film resistivity (lower leakage).The PLD obtained PLZT films compared to bulk material have higher E_c and tgδ while the ε values are lower. Sol-gel derived PLZT 9.5/65/35 film demonstrates dielectric characteristics more similar to those in bulk composition.Relative displacement in c-axis oriented PSN thin film (thickness 0.5 μm) is found ~0.01% at 300 kV/cm.

ACKNOWLEDGEMENTS

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IT4

Pulsed Laser Deposited Ferroelectric materials

A. Safari and C. Tantigate

Department of Ceramic Engineering and Center for Ceramics Research,
Rutgers University, Piscataway, NJ 08855

Introduction

There are several deposition techniques that have been developed and optimized for producing high quality thin films. Examples are metal organic chemical vapor deposition, pulsed laser deposition, plasma enhanced chemical vapor deposition, sputtering and sol-gel processing. Among these, pulsed laser deposition [PLD] is considered a simple and versatile technique for depositing a multilayer structure and obtaining epitaxial films with high deposition rates. Several ferroelectric materials such as $(Pb,Zr)TiO_3$ [PZT], $PbTiO_3$ [PT], $(Ba,Sr)TiO_3$ [BST] and $BiSr_2Ta_2O_9$ and superconducting films were prepared by PLD. There are several factors involved in the development of thin films by PLD that needed to be optimized to obtain high quality thin films. The typical parameters are the substrate temperature, the ambient pressure, the distance between substrate and target, the laser fluence and the density of target. Some of the factors effecting the quality of ferroelectric thin films prepared by PLD are summarized below. Recent advances in the development of ferroelectric thin films by PLD is reviewed.

Factors Effecting the Quality of the Films

- Effect of Substrate Temperature

Substrate temperature has a direct effect on the phase formation in the film especially for in-situ PLD. It also is an important parameter to optimize for a particular crystal structure and orientation. The thermal energy that the condensing species attains on the substrate surface allows for increased surface mobility, and energy for nucleation and growth of the film. For example, the perovskite phase formation of ferroelectric thin films prepared by in-situ PLD is dependent on the substrate temperature. Each material has its own specific temperature for nucleation and growth of the required phase, such as perovskite. The perovskite phase of PZT, PT, and BST are obtained at substrate temperatures in the range of 575°C to 600°C, 350°C to 450°C and 480°C to 600°C, respectively[1-3]. The effect of substrate temperature also contributes to the composition of the films. For instance, the Pb and Mg-deficiencies are observed in PZT and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [PMN] thin films at substrate temperatures above 600°C and 550°C, respectively[1,4].

- Effect of Ambient Pressure

The ambient atmosphere has the most influence on controlling film composition and uniformity. Studies of the ablated flux characteristics during PLD for multicomponent oxide showed a pressure dependence of the angular distribution of ablated species[5]. Most often in film deposition, an oxygen pressure is introduced. A higher oxygen pressure yields a narrower plume shape and results in nonuniform films with a low deposition rate. However, more volatile ion species are maintained at low oxygen pressures. The optimum condition for the amount of oxygen pressure during deposition needs to be studied for each deposited materials. The perovskite phase of PZT and PMN thin films are obtained at an oxygen pressure of 200 mTorr [1,4].

- Effect of the Distance Between Target and Substrate

The distance between target and substrate has a significant effect on the deposition rate. A large distance between the target and substrate results in low deposition rates. On the other hand, it produces more uniformly deposited films[6]. A smaller distance between the target and substrate may generate surface particulate in the film, which is generally observed in superconducting films of YBa_2Cu_3Ox [YBCO].

- Effect of Laser Fluence

The laser fluence is controlled by the variation of the spot size on the target and the laser energy. The spot size on the target is determined by the focal length of the focusing lens. There is a threshold for laser energy when interaction occurs with the target material. Above the threshold, the deposition rate is increased linearly with the laser fluence[7]. However if the laser energy is kept constant, a smaller spot size will yield a lower the deposition rate because of the broad of the angular distribution of the ejected materials. Film uniformity is also affected by the spot size. The smaller the spot size, the more spherical the shape of the plume of ablated material across the target, and consequently, a more even a distribution of material is obtained. The typical laser fluence for growing the ferroelectric films is the range of 1-2 J/cm^2.

- Effect of Target Density

There are two kinds of target materials used in PLD; pressed oxide and sintered pellets. Pressed oxides are reported to provide higher ion contents in the plume during deposition in comparison to the sintered pellets for PZT. The Pb-deficiencies are found in the films made from sintered targets as opposed to those made from the pressed oxide targets[8]. However, the high density of sintered targets is essential since it reduces the debris from the target which can deposit on the substrate surface. For typical sintered PZT target, the excess Pb is added in the compositions to compensate the Pb deficiencies.

Modification of PLD Technique

Although PLD has been successful in thin film deposition on a laboratory scale, commercialization of this technology still needs to be developed. There are two significant problems involved in thin film deposition by the PLD technique. One is the presence of particulates on the film surface and the other is the nonuniformity of the film thickness over large area.

The elimination of particulates has been studied extensively. The general technique used to eliminate the particulate is to reduce the laser power density by increasing the spot size. Other techniques to reduce particulate are spinning the target at a high velocity while focusing laser on the off centered target[9] or filtering to block large particles from depositing on substrate as shown in figure 1.

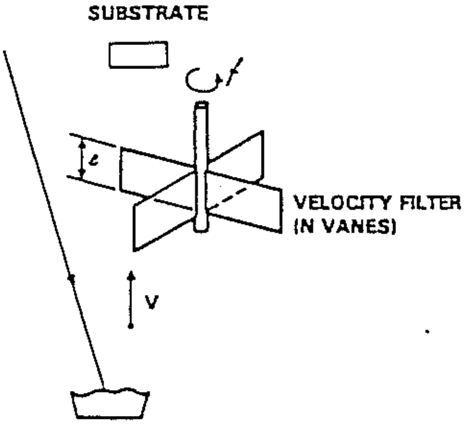

Figure 1 Schematic diagram of a velocity filter for eliminating particle[9].

Nonuniformity of the film over a large area was reported to be a crucial problem for applications of large area electronic devices applications. Three methods are reported to be successful for deposit films over large areas. These are "Off Axis", "Rotation /Translation" and "Raster" PLD. Uniform thin films of superconductors and ferroelectrics such as YBCO and $Bi_4Ti_3O_{12}$ have been deposited on the substrates with a diameter 50 to 100 mm. A comparison of these three techniques are shown in figure 2.

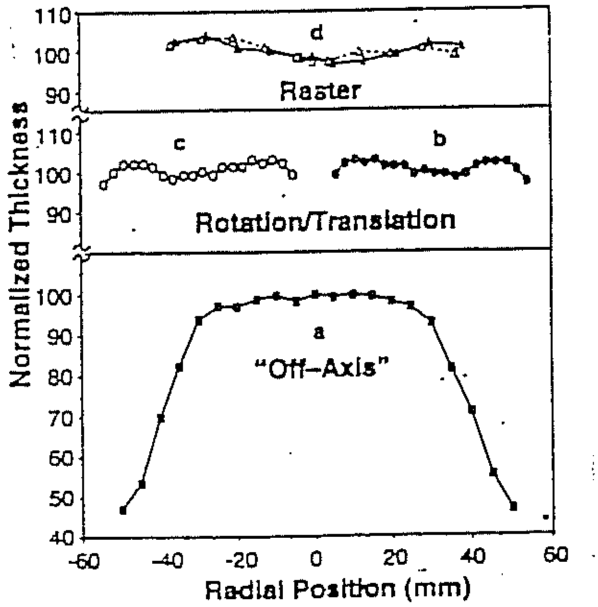

Figure 2. The comparison of the film thickness profiles obtained from "Raster", "Rotation/Translation", and "Off Axis" PLD over large area.

Recent Advanced in Ferroelectric by PLD

Research activities in ferroelectric thin films prepared by PLD has recently increased. The low temperature deposition of PLD makes it possible for the deposition of thin films consisting of volatile materials, especially perovskite Pb-based ceramics. PT is deposited using a second laser irradiating the surface of the substrate during deposition with a phase formation temperature below 400°C[2]. $(Pb,La)(Zr,Ti)O_3$ [PLZT] has been successfully deposited by PLD at a substrate temperatures of 520°C and an oxygen pressure of 200 mTorr[10].

Among Pb-based perovskite ferroelectrics, PZT is the most extensively studied by PLD. A great deal of research emphasizes on the preparation of PZT for DRAMs and FRAMs applications. The problem of fatigue in ferroelectric memory is under investigation. PLD has shown a great contribution on the fatigue studies of PZT thin films. Lee, et al. reported effect of crystalline quality and electrode materials on fatigue behavior. PZT has been deposited with epitaxial, highly oriented and polycrystalline structures on $SrTiO_3$(100), MgO(100), and *r*-plane sapphire, respectively. The results show better fatigue resistance in polycrystalline PZT films. However, electrode materials are reported to have a severe effect on fatigue[11]. In several reports, perovskite materials (e.g. $BaTiO_3$, $SrTiO_3$ and $BiTiO_3$) are used as template layers to promote development of perovskite phase on different kinds of substrates with different crystal structures. PZT thin films are successfully grown on Pt coated Si substrates using $BiTiO_3$ as a template layer. $BaTiO_3$ and $SrTiO_3$ are used to grow epitaxial MgO perovskite films on GaAs substrates[12].

For DRAMs applications, $(Ba,Sr)TiO_3$ has been prepared by PLD. The results show a dielectric constant of 330, a dissipation factor of 0.02, a charge storage of density of 36 fC/μm^2, and a leakage current of $2x10^{-7}$. These characteristics are acceptable for the ULSI DRAM[13].

$SrBi_2Ta_2O_9$ (SBT) is a promising material for FRAMs. It was first synthesized by sol-gel technique and shows no fatigue upto 10^{10} switching cycles. SBT possesses a perovskite layer structure and has a general formula of $(Bi_2O_2)^{2+}$, $(A_{x-1}B_xO_{3x+1})^{2-}$, where A and B represent ions of appropriate size and valence. For x=2, the crystal structure consists of two perovskite like layers along the c-axis, infinite in two dimension and alternating with a layer of $(Bi_2O_2)^{2+}$. With the arrangement, the O-Ta-O chains of perovskite along c-axis are interrupted by (Bi_2O_2) layers, but form a continuous chain along the plane perpendicular to the c-axis[14]. Recently, layered perovskite SBT thin films were grown by PLD technique. The perovskite structure was obtained at a substrate temperature of 535°C and oxygen pressure of 300 mTorr on a platinized Si/SiO_2 wafer and then annealed at 800°C. The pulsed laser deposited SBT films exhibit fatigue resistance up to 10^{10} switching cycle with a remanent polarization of $2P_r = 8\text{-}13\ \mu C.cm^{-2}$;however, the leakage current needs to be improved[15]. Recently, it has been reported that a c-axis oriented $SrBi_2(Ta_xNb_{2-x})O_9$ where $0< x< 2$ has been successfully grown on MgO(100)/Pt(100) and Pt/Ti/ SiO_2/Si substrates[16]

For electro-optic and memory applications, $Bi_4Ti_3O_{12}$ has been grown on indium tin oxide substrates at 650°C[17]. C-axis oriented ZnO thin films were successfully grown at substrate temperatures of 180 to 400 °C in Ar and $Ar+O_2$[18].

Electrode Materials

The electrode material is one of the most important issues for fatigue in ferroelectric films. Pt is the most common electrode for capacitor cells because of its high conductivity ($\approx$5-20 $\mu\Omega cm^{-1}$) and its inertness to oxidation. However, Pt electrodes occasionally have problems of hillock formation and interdiffusion between the electrode layer and the silicon substrate. The formation of hillocks at the Pt surface causes dielectric breakdown in the films.

Recently several oxide electrodes are being used such as RuO_2, YBCO, LSCO and ITO. RuO_2, LSCO and YBCO showed better fatigue characteristics compared to Pt electrodes. The room temperature resistivity of metal oxides are in the range of a few hundred $\mu\Omega$cm. For example, LSCO has resistivity of 90 $\mu\Omega$cm. RuO_2 would be preferred over the YBCO as an electrode material because of its lower resistivity (at ambient temperature), chemical compatibility with Si, and its lower processing temperature. It has been reported that capacitors of RuO_2/PZT/RuO_2 exhibit no fatigue up to 10^{12} cycles. However, RuO_2 is not a perovskite cubic structure like most of ferroelectric materials, and therefore the deposition of epitaxial films for high density memory devices will be extremely difficult.

LSCO and YBCO have been developed by PLD technique and are becoming promising electrode materials for ferroelectric films. Both posses perovskite-structure and lattice parameters close to those of most of Pb-based ferroelectric materials. YBCO has a lattice parameter of 3.8 to 4.2 Å which is a good match with PZT films (lattice parameter 4.036 Å) and therefore epitaxial PZT is obtained, and good fatigue resistance is exhibited. LSCO has received more attention lately because its has a higher room temperature conductivity compared to YBCO. PZT films prepared with LSCO bottom electrode showed fatigue free up to 10^{12} cycles. In the fatigue issue, oxide electrodes are under investigation to replace the Pt electrode.

The appropriate electrode material applied by a suitable technique can enable fatigue rates to approach the intrinsic rate of the ferroelectric materials. It has been reported that the electrode material together with deposition method has a pronounce effect on the fatigue resistance. Sputtered

Au showed superior fatigue resistance in PLZT compared to co-fired silver-paste electrode. Polishing the evaporated In-Ga electrode promoted an improved film-electrode contact, and as a result, there is no fatigue was detected up to 10^{-9} cycles[19].

The electrode materials mentioned earlier can be used as both the bottom and top electrode. It is also evident that the bottom electrode affects the device resistivity, although the exact reason has not been determined. LSCO top electrodes showed lower resistivities compared to Pt due to its lower work function. The results from hysteresis and fatigue measurements show that the bottom electrode and top electrode play a role in determining the ferroelectric device properties. The bottom electrode controls the phase and orientation of PZT and affects properties such as P_r, E_c, and resistivity. On the other hand, the top electrode affects device resistivity. For studies of fatigue, using oxides as both top and bottom electrodes has yielded better fatigue behavior than metal electrodes[20]. Moreover, the fatigue process is described to rely on oxygen vacancy movement and build up at (or near) interfaces. Therefore oxide electrodes would then be necessary to minimize the polarization fatigue. The oxide electrode may act as either a source or sink for oxygen vacancies moving through the PZT under a switching field, and in this case, fatigue free films were obtained. However, fatigue reduction could be related to the interface defect density and Schottky barrier heights as well[21].

Summary

Recent research and development has shown that PLD is one of the most promising techniques for ferroelectric thin film research. The simplicity, the low temperature processing, and the versatility of this method have opened up the field of deposited materials. There are only a few factors that needed to be optimized to obtain high quality films. The modification of PLD makes it possible for depositing uniform films without particulates over a large area. PLD is consider as a potential technique for the deposition of ferroelectric thin films, especially those of Pb-based composition. In addition, the ability to grow multilayer and heterostructure films extends the variety of electrode materials available to fatigue related.

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Contributed Talks

Ferroelectric Characterization of sol-gel thin film modified $PbTiO_3$ films

J. Mendiola and P. Ramos

Instituto de Ciencia de Materiales de Madrid (CSIC).
Cantoblanco 28049 Madrid (Spain)

Introduction

The electrical characterization of ferroelectric thin films, usually consist to measure the hysteresis loop and switchig currents and the time dependence.

Remanent polarization, P_R , obtained from hysteresis loops, normally depends on the type of signal and of the previous electrical treatment used in order to stabilize, or condition the sample [1]. P_R values are frequently overestimated, and not coincident with those obtained from switching currents[2], being probably due to the measuring method.

We report hear the effects of a previous electrical treatment on the measurements of hysteresis loops and switchig currents in samples of Ca modified lead titanate.

An electric signal is applied before making ferroelectric measurements, in order to act on the state, probably with defects, of the sample. The action of the field on the electric carriers which were generated during the thermal treatment of the film could be explain the observed effects. The difference between the values of remanent polarization obtained from the two methods of measurement is also pointed out.

Sample preparation

The samples studied have been obtained from precursor solutions of nominal composition $Pb_{0.76}Ca_{0.24}TiO_3$. They were synthesized by the sol-gel method [3]. Solutions were deposited by spin-coating on $Pt/TiO_2/SiO/Si(100)$ substrates. For the crystallization of the films, the final treatment temperature (650°C) was achieved with different heating rates:° 5 C/min., 40°C/min. and ≈ 500°C/min., which will hereafter be called A, B and C. The thickness of the films is about 500 nm, and the average grain size of about 100 nm and decreases when the heating rate increases. X-ray diffractograms only show perovskite phase, and a small amount of pyrochlore phase which is almost absent in sample C. Analyses by Auger electron spectroscopy [4], RBS and lattice parameters obtained by GIXRD [5] point to a deficiency in Pb, probably caused by a loss of PbO during the thermal treatment. Recent samples have been prepared by puting a 10% of PbO into the precursor solutions to improve the stoichiometry.

Experimental results

Top platinum electrodes of 0.5 mm diameter were sputtered on the surfaces of the films. Measurements of switching currents and hysteresis loops were made. For the former, a sequence of square pulses was applied. After 10^4 poling pulses of -320 kV/cm

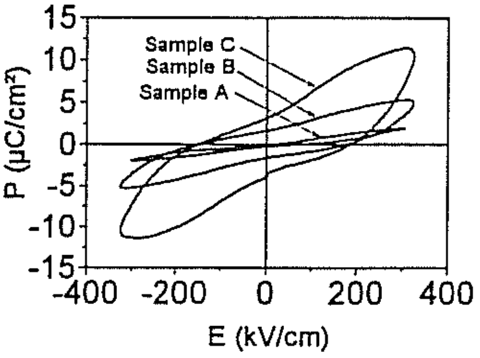

Figure 1.- P-E hysteresis loops (compensated) obtained *before* the electrical treatment.

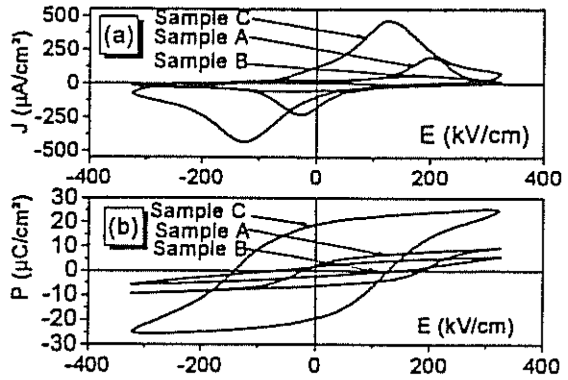

Figure 2 a) I-E curves from which loops are obtained b). P-E hysteresis loops (compensated), obtained *after* the electrical treatment.

amplitude and 200 µs width, separated by 20 µs intervals, two reading pulses were used for measuring current curves. Rise time of the pulses was 10 ns, and the time elapsed between polarization and measurement was 300 ms. Thus, the remanent polarization P_{sw}, and the switching time t_s , can be calculated.

To obtain hysteresis loops a sinusoidal signal was used of 320 kV/cm amplitude at different frequencies.

The hysteresis loops obtained at 1Hz from the virgin samples do not show clear signs of ferroelectricity, but rather a considerable contribution of leakage currents (Fig 1); the current measurements do not show any switching phenomena. Nevertheless, if the same samples are subjected to an electrical treatment, consisting in the application of a square wave of 1 Hz and ± 320 kV/cm amplitude for 60 seconds, the hysteresis loops measured are nearer to the saturation (Fig. 2), with the contribution of leakage current drastically reduced and with better defined coercive fields. Also switching currents can be measured and thefore switching times are clearly determined (Fig 3).

The improvement achieved with the electrical treatment with square wave is not lasting: after some seconds, P_{sw} desappears. However, the same experiment, performed with a sinusoidal wave of the same frequency and a ± 500 kV/cm amplitude, gave rise to more persistent effects, with switching taking place for over 30 minutes after the electrical treatment (Fig 4). In a determine C sample higher retention was measured: from 8 to 2 μCcm^2 in 5 months.

In order to know the effect of frequency, hysteresis loops were traced at different frequencies, for a C sample, after being treated with a square wave (Fig 5). The contribution of leakage currents decreases with frequency.

Discussion

The decrease in Pb content observed next to the two interfaces (film-substrate and film-air), could be ascribed to losses of PbO during thermal treatment, giving rise to Pb and O vacancies. Also, the existence of other defects (micropores, dislocations, etc.) cannot be discarded.

On the other hand, small grains may difficult the movment

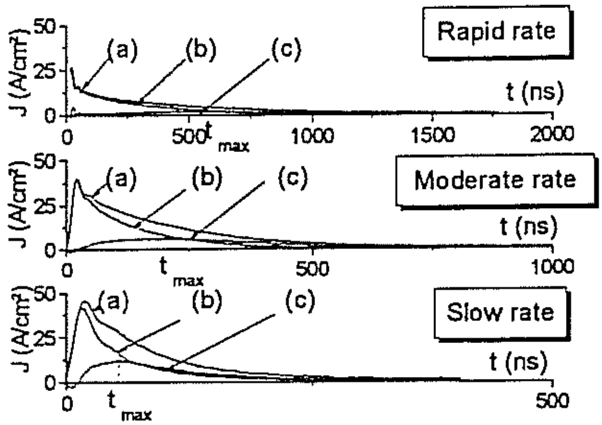

Figure 3.-Currents originated by the two measurement pulses applied to the sample after the electrical treatment. The difference between them is also represented

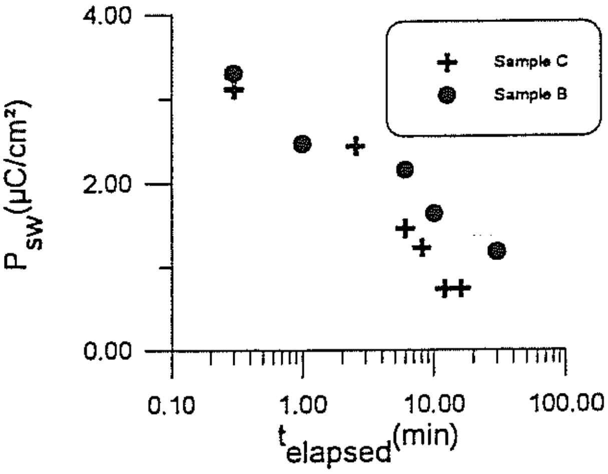

Figure 4.- Variation of the remanent polarization, P_{sw}, calculated from switching current curves, as a function of the time elapsed after the electrical treatment with a sine wave, for samples B and C.

of 90º domain walls due to a clamping effect. Furthermore, the presence of charged defects, other than O and Pb vacancies, may also hinder the inversion of domains in samples in their virgin state. This would explain the poor ferroelectric character shown by the hysteresis loops traced before the application of the electrical treatment. The charge involved in them could be almost exclusively due to leakage currents.

The high electric fields applied during the previous electrical treatment (±500 kV/cm) could move the charged defects, causing some deaging or conditioning of the sample. Thus , leakage currents, which contribute to the loops in the virgin state, are reduced, and domain become more free to move, and their switching is facilitated, being the hysteresis loops of better quality.

The no permanent effect may be consedered as an evaluation of the retention of switched polarization. It has been measured that, after 24 hours, the loop deteriorates markedly, but is recovered after repeating the electrical treatment. This reversibility is not fully understood. The study is being continued in order to determine the dependence on electrical tretment parameters.

Table I shows values of P_r and $_cE$, determined from hysteresis loops, and those of P_{sw} and t_m, from switching current curves. Values of P_{sw} are always lower than those obtained from the hysteresis loops (P_r). The discrepancy is due to differences between the two methods of measurement.

TABLE I. Hysteresis loop and switching data

	2|Pr| (µC/cm²)	(|Ec⁺|+|Ec⁻|)/2 (kV/cm)	+Psw (µC/cm²)	t_{max} (ns)
SAMPLE A	8.0	115	0.6	50
SAMPLE B	3.7	114	1.3	66
SAMPLE C	38.1	126	9.5	280

The values of P_{sw} may be considered as the highest possible, because in switching measurements, only charges of ferroelectric origin make a net contribution; nevertheless, between the two reading pulses may occur a switching back of domains, being the P_{sw} values lower. On the other hand, P_r values have other contributions, because integration times are much larger. Any possible type of leakage should in principle be considered. Given the low value of the grain size/thickness ratio, the probable causes of leakage could be in the grain boundaries potential barriers, and their interaction with charged defects. The hysteresis loops measured at different frequencies support such hypothesis since the contribution of the leakage currents to the P_r values decreases cosiderably with frequency. On the other hand, since the grain size of sample C is smaller than A's, the number of grain boundaries across the sample will be grater for C and this implies greater dificulty-for the switching of domains, and therefore, greater switchig times, according to the Larsen's model[6].

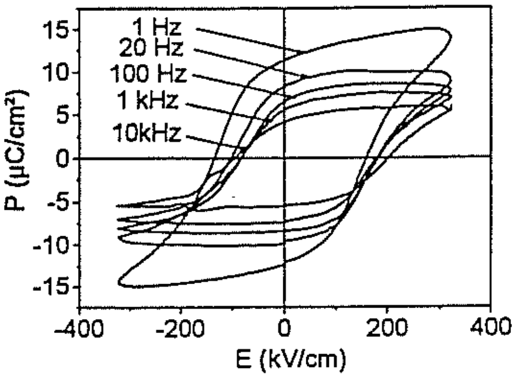

Figure 5.- Hysteresis loops of sample C, traced at several frequencies after treatment with square wave

Since a similar behaviour has been observed in samples with a 10% of Pb in excess in the precursor solution, we think , the most important to measure high ferroelectric characteristics in our polycristalline films, is to apply some previous treatment for preconditioning or stabilizing the sample. Therefore, the type of defects implied in masking ferroelectric values do not seem to be mainly related with stoichiometry, suspecting from the interfaces as source of electric carriers.

Acknowledgements

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MICROSTRUCTURAL STUDIES OF SOL-GEL PROCESSED Sm MODIFIED LEAD TITANATE THIN FILMS

E. Snoeck, J. Ricote[†], R. Coratger, L. Pardo[†].

Centre d'Elaboration de Materiaux et d'Etudes Structurales. CNRS.
29 rue Jeanne Marvig, 31055 Toulouse Cedex (FRANCE).
[†]Instituto de Ciencia de Materiales de Madrid. CSIC.
Cantoblanco, 28049 Madrid (SPAIN).

Abstract.

The microstructure characterization of the sol-gel processed Sm modified lead titanate (nominal composition $(Sm_{0.08}Pb_{0.88})TiO_3$) thin films is carried out using Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The ferroelectric films are deposited onto (100) oriented $Si/SiO_2/TiO_2/Pt$ substrates by spin coating method and are crystallized by a conventional thermal treatment at 550°C or 700°C (heating rate of $10°C.min^{-1}$).

The close inspection of the structure and composition of the different phases allows the study of their crystallization process. As reported in Figure 1, the films present a complexe microstructure consisting in some large regions, with shape similar to "rosettes", surrounded by a porous phase.

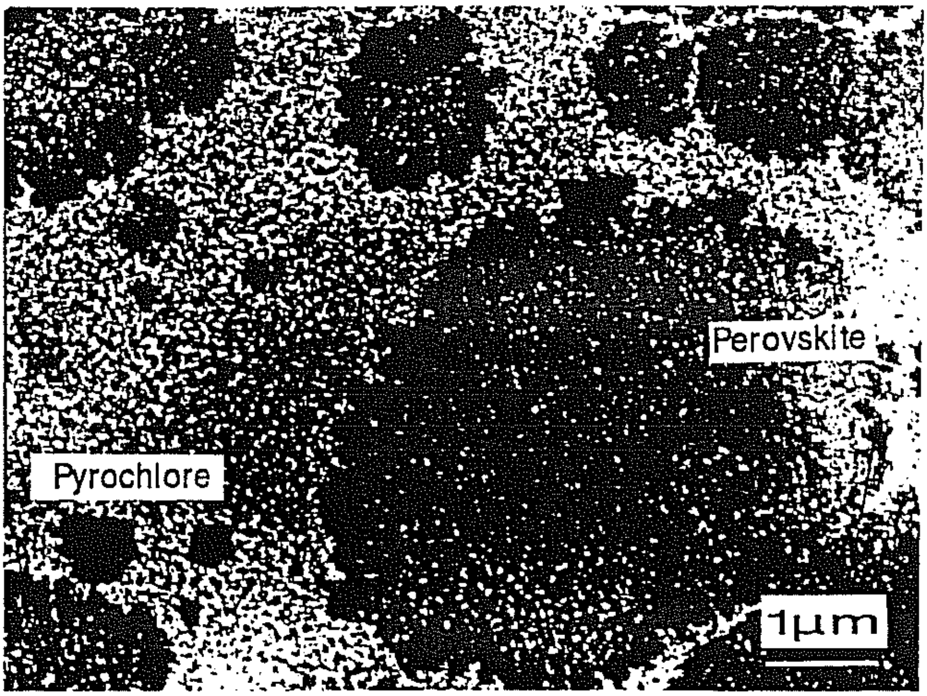

Figure 1 : Low magnification bright field image revealing the microstructure of a PTS thin film crystallized at 700°C.

Electron diffraction experiments performed on rosette-shaped regions evidence the expected ferroelectric perovskite phase. AFM and TEM experiments show that these "rosettes" are constituted by small crystallites of about 100nm diameters wich grow from the center to the edges.

The surrounding porous phase is also pollycristalline and EDS measurements reveals that it is lead deficient. Previous X Ray diffraction studies have evidenced the appearance of pyrochlore phases suggesting that this surrounding porous second phase is a non-ferroelectric pyrochlore one. Nevertheless, it was not possible to completely identify the structure and nominal composition of this second phase, neither from the XRD nor from the electron diffraction results. The origin of this Pb-deficient phase can be attributed to the existence of Pb-poor regions in the film, either due to an inhomogeneus distribution of Pb during the deposition, or to Pb losses resulting from the thermal treatment. However, these secondary phases can be completely eliminated by adding excess of PbO.

The use of different precursor solutions (water dissolved samarium acetate or diol-dissolved samarium acetylacetonate).does not produce any significant effect on the composition and the structure of the phases. However, rising the temperature of the thermal treatment (from 550°C to 700°C) increases the content of porosity inside the rosettes and sharpens the grain boundaries.

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Piezoelectric measurements and piezoelectric fatigue in PZT thin films

A.L.Kholkin, E.L.Colla, K.G.Brooks, A.K.Tagantsev, D.V.Taylor, and N.Setter

Laboratoire de Céramique, Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne, Switzerland

Experimental set-up is developed on the base of double-beam laser interferometer, which is capable of measuring ultra-small electric field-induced displacements in piezoelectric thin films. The interferometer resolution (~10^{-4} Å) is significantly improved in comparison with previously reported systems. The interferometer technique is succesfully applied for the piezoelectric characterization of sol-gel derived PZT films. It is shown that piezoelectric coefficients of 100-150 pm/V and strains of (2-3)10^{-3} can be achieved with the compositions near morphotropic phase boundary. Piezoelectric fatigue is studied in sol-gel PZT films. It is found that bipolar fatigue induces significant polarization offset due to the locking of ferroelectric domains in preferable orientations. Piezoelectric fatigue under unipolar electric stress is described as a built-up of internal bias field due to the injection of charge carriers into the film.

1. INTRODUCTION

Ferroelectric thin films are very attractive for use in microelectromechanical systems (MEMS) because of their superior piezoelectric properties as compared to conventional ZnO films. Recently, several viable microelectromechanical devices based on ferroelectric thin films have been demonstrated such as ultrasonic piezoelectric motors, pressure sensors and sensors for AFM (see e.g. [1-3]). The increasing range of piezoelectric applications of ferroelectric films requires an adequate measurement technique which allows their non-destructive piezoelectric testing. Another important problem is the degradation of piezoelectric response, which has to be evaluated for a particular stressing conditions.

This paper discusses different aspects of piezoelectric characterization of ferroelectric thin films. An interferometric technique is applied for the investigation of piezoelectric properties of PZT films and degradation mechanisms of piezoelectric response.

2. EXPERIMENTAL TECHNIQUE

Several techniques has been previously employed to determine piezoelectric properties of bulk ferroelectric materials. However, it is difficult to apply the conventional techniques for the investigation of piezoelectric properties of ferroelectric thin films because of the small thickness of the films and clamping effect of the substrate. For example, the resonance-antiresonance technique, which is frequently used to evaluate the piezoelectric properties of bulk materials materials, requires the measurements in the GHz range and involves significant difficulties.

The measurements of converse piezoelectric effect offer the great advantage since piezoelectric displacements can be locally determined under the low driving field in the broad frequency range. The low level of the displacements in thin films necessitates the use of a very precise interferometric technique. Usually, a resolution of about 10^{-2}-10^{-1} Å is needed to measure the low-field piezoelectric coefficients in ferroelectric thin films. Another problem is the bending motion of the substrate which may contribute to piezoelectric displacements if only the movement of the film surface covered by the top electrode is monitored [4]. Therefore, a single-beam interferometric technique which has been recently proposed for piezoelectric measurements in ferroelectric thin films [5] has to be modified to separate the bending motion of the substrate from "true" piezoelectric response

To solve these problems, we developed a sensitive stable double-beam interferometer which is capable of measuring ultra-small electric field-induced displacements in piezoelectric thin films [4]. The symplified optical arrangement of the double-beam interferometer is shown in Fig.1. By using the polarized beam-splitters and $\lambda/4$ plates the laser beam probes both the top electrode and the back side of the substrate. Thus any bending of the substrate which produces the increase of the optical path of one of the beams is exactly compensated by the equal decrease of the optical path of the second beam.

The interferometer performance was significantly improved in comparison with previously reported system [6]. For example, the interferometer resolution was increased by more than an order of magnitude which made it possible to determine electromechanical coefficients of thin films under low driving field conditions. Another advantage of the interferometer is the enhanced stability which permits the long-term measurements such as aging studies [7].

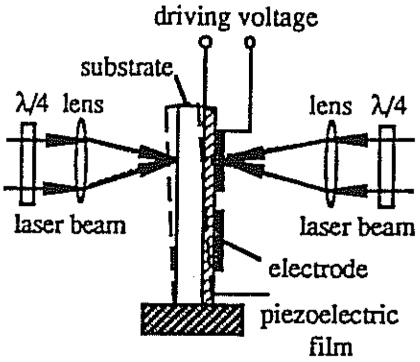

Fig.1. Double-beam optical arrangement for interferometric measurements of small electric field-induced displacements in piezoelectric thin films.

Fig.2 demonstrates the capabilities of the interferometric technique to measure the small electric field-induced displacements in PZT films. The variation of both piezoelectric (1st harmonic) and electrostrictive (2nd harmonic) displacements under low AC field is shown as a function of DC bias field. A very low noise level (about $2\ 10^{-4}$ Å in this case) allows an investigation of both piezoelectric (d_{33}) and electrostriction coefficients (M_{11}) of the PZT film.

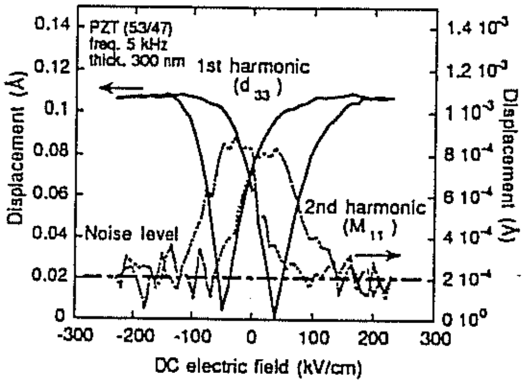

Fig.2. Electric field-induced displacements (1st and 2nd harmonics) as a function of DC electric field in PZT thin film.

Another important feature of the interferometric technique developed in this study is the possibility to directly measure the displacements without using the lock-in technique. The increased sensitivity and relatively low noise level enable the measurements of time-dependent strains by using a digital oscilloscope. Thus the interferometer could be used as a strain gauge. Fig. 3 shows a typical strain-field dependences in sol-gel PZT films obtained under different electric fields. For the low applied field, the interferometer response follows the driving field and pure piezoelectric effect is observed. Correspondingly, strain is a linear function of electric field. The piezoelectric coefficient can be derived from the slope of this line. If the applied electric field is higher than the coercive field in the PZT film, ferroelectric domains start to switch. Therefore, a typical butterfly-type strain hysteresis loop is observed.

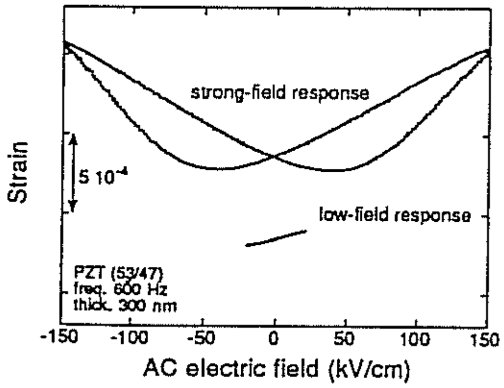

Fig.3. Typical strain-field response of the PZT film under low- and high applied electric field.

3. PIEZOELECTRIC PROPERTIES OF SOL-GEL PZT FILMS

The interferometric technique developed in this study was applied for the evaluation of piezoelectric properties of PZT films. PZT thin films of various compositions were prepared on platinized Si substrates by sol-gel technique using a standard method described by Budd et al. [8]. The film microstructures were columnar and mostly (111) textured. A detailed description of the sol-gel process can be found elsewhere [9].

Fig.4 shows the effective piezoelectric coefficient d_{33} of PZT films as a function of Zr content for several selected compositions. It was found that d_{33} exhibits a pronounced peak near the morphotropic phase boundary. The position of the peak corresponds approximately to that of the PZT ceramics, however the values of d_{33} were found to be lower than those of bulk PZT [10]. The lower values of d_{33} can be satisfactory explained by the clamping effect of the substrate [11]. Obviously if the transverse strain is constrainted by the substrate the longitudinal deformation is expected to be lower than for the case of free material since d_{33} and d_{31}

piezoelectric coefficients have the opposite signs.

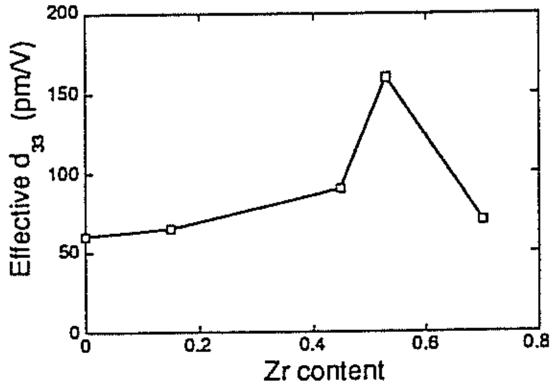

Fig.4. Effective piezoelectric coefficient in the PZT films as a function of Zr content.

It was found that strain under the fixed electric field also maximizes for the PZT compositions near the morphotropic phase boundary. The maximum strain which can be attained in thin films is limited by their dielectric strength which is influenced by the film thickness, electrode area, electrode material etc. (see, e.g. [12]). The maximum strain for sol-gel PZT films used for this study was about (2-3) 10^{-3}.

4. PIEZOELECTRIC FATIGUE

The evolution of piezoelectric coefficients under bipolar and unipolar cycling in sol-gel PZT films was determined with the purpose to elucidate the nature of the polarization fatigue and to evaluate the endurance of PZT films for MEMS applications [13]. The films used for this study exhibited a pronounced polarization fatigue after about 10^4-10^5 bipolar pulses. This behaviour is typical for PZT films with Pt electrodes (see, e.g. [14]). Fig.5 shows d_{33} piezoelectric hysteresis loops taken for virgin and fatigued PZT capacitors. It is clearly seen that bipolar cycling results not only in the decrease of maximum and remanent piezoelectric coefficients (as expected from polarization measurements) but also in a strong shift of hysteresis curves along d_{33}-axis. As the result of this offset, both coercive fields become negative and negative remanent d_{33} becomes positive. This behaviour was observed in other sol-gel films having different microstructures and fatigue endurances and seems to be a general feature of piezoelectric fatigue. An apparent conclusion was made that polarization switching creates permanent (non-switchable) polarization which offsets piezoelectric hysteresis loops. The origin of the polarization offset, which can be as large as two times the remaining switchable polarization in PZT films, is presumed to be the locking of ferroelectric domains in the preferable orientations. Locked domains, which can not anymore contribute to switching, still contribute to d_{33} resulting in the offset of piezoelectric hysteresis loops. This strongly supports the pinning mechanism of fatigue (see, e.g. [15]). It should be emphasized that the effect of fatigue-induced polarization offset can not be obtained from conventional polarization measurements since they give only the change of switchable polarization. Only the measurements of low-field piezoelectric coefficient, which reflects the net polarization in the PZT film, provide information about the locked ferroelectric domains.

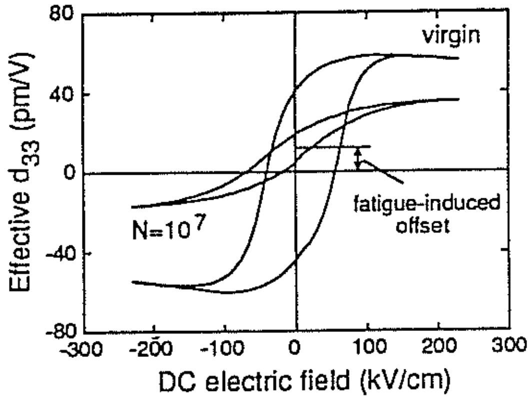

Fig.5. d_{33} piezoelectric hysteresis loops for virgin and fatigued ($N=10^7$) PZT (45/55) capacitors.

An important issue concerning the application of PZT films in MEMS is the endurance of piezoelectric coefficients with respect to unipolar fatigue. Under normal operating conditions the films will never be switched, therefore the bipolar fatigue is of less importance.

Fig.6 compares the change of the remanent piezoelectric coefficients during bipolar and unipolar fatigue in PZT films. It was found that the degradation in the case of unipolar fatigue is much smaller than that under bipolar stressing conditions. This behavior is compatible with the behaviour of switching polarization. Fig.7 shows the change of the coercive fields measured with piezoelectric effect during unipolar fatigue. It may be inferred that the main effect of the unipolar fatigue is the shift of piezoelectric hysteresis loops along the field axis This behaviour is described as the built-up of internal bias field during unipolar fatigue. The internal bias field, which direction coincides with direction of external field, is assumed to be a result of injection of charge carriers over the barrier between the metal electrode and PZT film. These carriers become immobile due to the trapping process and form space charge layer near the film-electrode interface. During fatigue process, the space charge internal field shifts the coercive fields measured with piezoelectric effect.

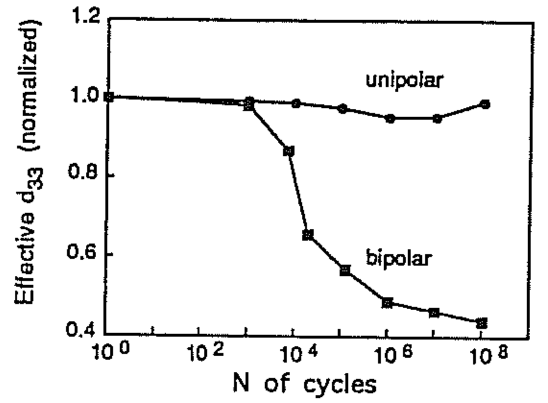

Fig.6. Comparison of bipolar and unipolar piezoelectric fatigue in PZT (45/55) films.

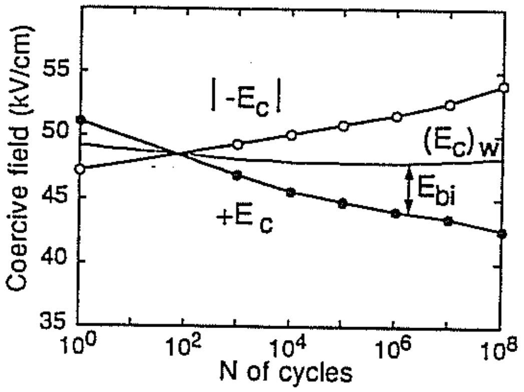

Fig.7. Evolution of the coercive fields for piezoelectric effect under unipolar cycling in PZT (45/55) films.

5. CONCLUSIONS

In this work, an experimental set-up has been developed on the base of the double-beam laser interferometer, which is capable of measuring ultra-small electric field-displacements in piezoelectric thin films. The interferometer resolution was significantly improved in comparison with previously reported systems. The interferometer technique was succesfully applied for the characterization of PZT films of different compositions. It was shown that effective piezoelectric coefficients of 100-150 pm/V and strains of (2-3)10^{-3} can be achieved with the compositions near the morphotropic phase boundary.

Piezoelectric fatigue has been studied in sol-gel PZT films. It was found that bipolar fatigue induces a significant polarization offset due to the locking of ferroelectric domains in preferable orientations. The main result of the unipolar fatigue is the shift of hysteresis loops along the field axis which is considered as the built-up of the internal bias field due to injection of charge carriers.

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"Current studies on Ferroelectric Thin Films in Stockholm"

Prof. K.V. Rao. Royal Institute of Technology (Sweden)

Electrical properties of lithium tantalate thin films on silicon substrates

CT5

C.-H. Kohli, P. E. Schmid, F. Lévy

Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne,
CH-1015 Lausanne, Switzerland

Thin films of lithium tantalate have been deposited by RF sputtering on RuO_2-coated silicon substrates. The dielectric properties and the resistivity of the films have been investigated at various frequencies and temperatures. At room temperature and 1 kHz the dielectric constant is 40 and the resistivity is 1.5×10^{8} Ωcm. The pyroelectric responses of lithium tantalate thin films either unpoled or poled at 40kV/mm for 60s have also been observed. A high pyroelectric coefficient of 5×10^{-8} C/cm^{2}K is obtained at room temperature.

Introduction

Ferroelectric perovskites have been applied to many useful electronic and optical devices utilising their excellent dielectric, piezoelectric and optical properties[1,2]. In the area of integrated devices, ferroelectric thin films in demand. In the work presented here, the emphasis was set on lithium tantalate pyroelectric thin films. We have investigated the electrical properties of these thin films deposited on RuO_2-coated silicon substrates.

Experimental procedure

Lithium tantalate thin films were fabricated using the RF sputtering technique. The target was a lithium tantalate ceramic disk, 60 mm in diameter and 8 mm thick. The films were deposited on $Si|SiO_2|RuO_2$ substrates held at 320°C. The as-deposited film was amorphous. A rapid thermal anneal (RTA) were carried out in an oxygen flow to obtain the crystalline phase. After the heat treatment, the films are polycrystalline with a typical grain diameter of 200nm.

The electrical measurements were carried out in the sandwich configuration. Upper Au, Ni or RuO_2 circular electrodes were evaporated or sputtered on the lithium tantalate films. The diameter of these upper electrodes was 0.8mm. The film resistivity and the dielectric properties were measured with a Hewlett-Packard impedance analyser, Model 4192A, from a frequency of 500Hz up to a frequency of 1MHz. For the measurement of the temperature dependence of the permittivity and resistivity, the sample was heated in an air furnace.

The pyroelectric measurements have been performed with the quasi-static method[3]. The thermal radiation was produced by a resistive Joule heater. Sinusoidal, triangular or rectangular voltages pulses were generated by a signal generator. The pyroelectric current and the temperature at the surface of the film were measured as a function of time. The current was measured across the film and recorded by a Keitheley 6517 electrometer. The temperature was recorded at the surface of the sample by a Pt100 probe. The film thickness was measured with an Alphastep profilometer.

Results

Dielectric constant

The relative permittivity as a function of frequency for different film thicknesses and different upper electrodes are shown in Fig. 1 and Fig. 2, respectively. The dielectric constant decreases with frequency and increases with film thickness. At 1kHz the relative permittivity is 40 for a 620nm thick film. This value is comparable with the lithium tantalate bulk dielectric constant of 45. Fig. 2 shows that for the nickel upper electrodes the relative permittivity decreases more rapidly than for ruthenium oxide or gold. The dielectric constant in presence of a ruthenium oxide electrode is larger than with a gold electrode for all the frequencies swept.

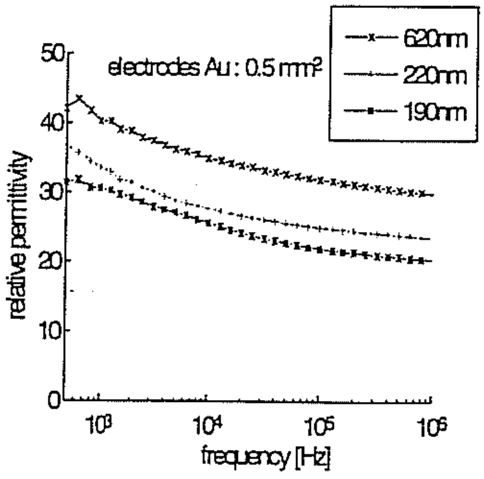

Figure 1. Dielectric constant vs. frequency for different thicknesses of lithium tantalate films measured at room temperature.

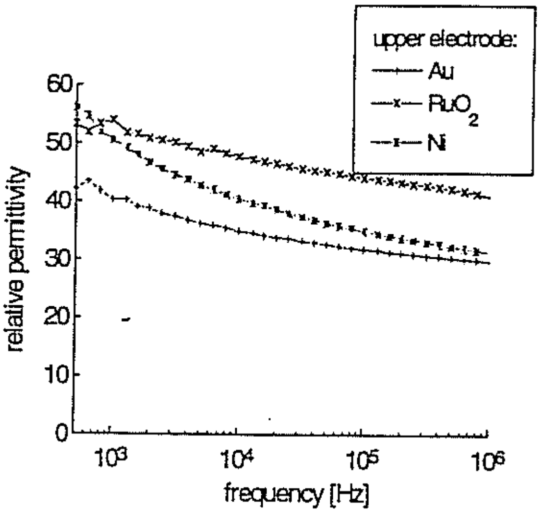

Figure 2. Dielectric constant vs. frequency for lithium tantalate films (620nm) with different electrodes.

The variation of the dielectric constant with temperature is presented in Fig. 3. The dielectric constant increases with temperature, and reaches a maximum value between 550° and 610°C. The maximum value indicates that the lithium tantalate thin film Curie temperature is about 600°C which compares well with the single crystal value of 615°C.

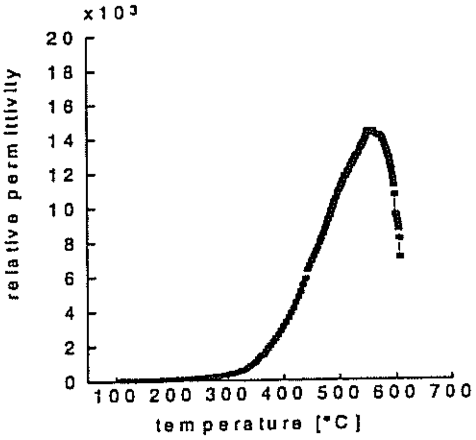

Figure 3. Dielectric constant vs. Temperature measured at 10kHz.

Resistivity

Fig. 4 shows the resistivity as a function of frequency for different thicknesses. The resistivity decreases with frequency like ω^{-p} with a value for p of 0.7. No dependence with thickness is observed. At 1kHz, the resistivity is $2x10^8\Omega$cm.

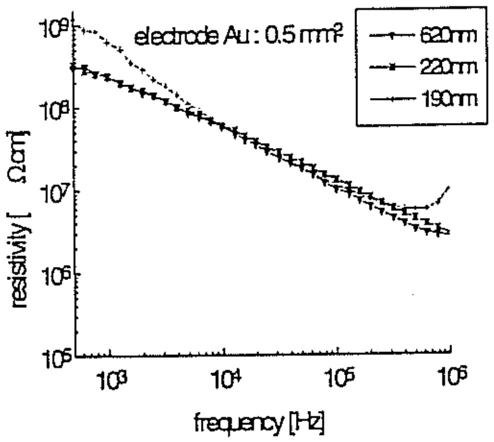

Figure 4. $LiTaO_3$ thin films : Resistivity vs. frequency for different thicknesses.

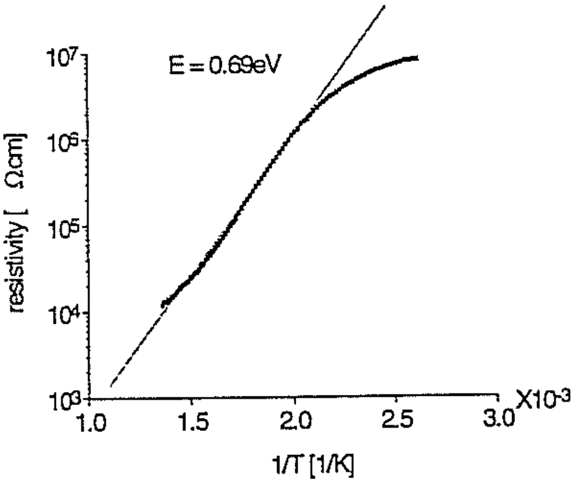

Figure 5. Resistivity as a function of 1/T for $LiTaO_3$ films measured at 10kHz.

The resistivity versus reciprocal of temperature is given in Fig. 5. The measurement was carried out at a frequency of 10kHz. The resistivity decreases with temperature. From the plot in Fig. 5, an activation energy of 0.69eV is calculated.

Pyroelectric properties

In Fig. 6, the response current for an unpoled film, proportional to the time-derivative of the temperature, demonstrates the pyroelectric properties of the lithium tantalate films. The pyroelectric coefficient of the film is 30μC/cm^{2}K, about one order of magnitude smaller than the pyroelectric coefficient of lithium tantalate single crystals.

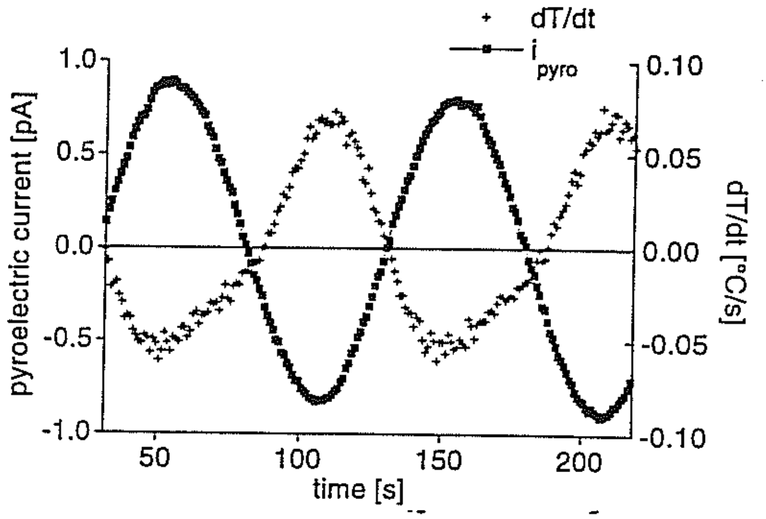

Figure 6. Pyroelectric current and dT/dt vs. time for $LiTaO_3$ thin films unpoled.

After poling at 40kV/mm for 60s, the pyroelectric current response is increased. The pyroelectric coefficient of the poled film is 500μC/cm^{2}K, of the same order of magnitude as the pyroelectric coefficient of the bulk.

Conclusion

The dielectric constant of lithium tantalate thin films is comparable to the dielectric constant of single crystals. The Curie temperature of the thin film, about 600°C, is approximately the same as in the bulk. The ac resistivity as a function of 1/T shows an activation energy of 0.69eV, and at room temperature the resistivity is $2\times10^8\Omega$cm. The pyroelectric coefficient for a poled film is of the same magnitude as for a lithium tantalate single crystal.

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COST 514 Workshop, Madrid 4-5 March 1996

Thermal Annealing of Sputtering and RIE Induced Defects in PZT Ferroelectric Capacitors

Dirk J.Wouters, Eun-Gu Lee, and Geert Willems
IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

1. INTRODUCTION

Pt/PZT/Pt ferroelectric capacitors are investigated for Non-Volatile Memory application (FERAM). $PbZr_{.x}Ti_{.1-x}O_3$ (PZT) is an interesting ferroelectric material because it has very high remanent polarization (P_r) values, and crystallizes at relatively low temperatures. We focus on high Ti-content tetragonal materials as very rectangular hysteresis loops can be obtained.

Pt is used as the electrode as it is the most commonly available contact material, although it is known to result in Pt/PZT/Pt capacitors with limited endurance. The Pt is typically deposited using a (magnetron) sputtering process. Furthermore, for a high-density memory process, patterning by dry etching (Reactive Ion etching, RIE) i.o. alternative shadow-mask or lift-off techniques has to be used.

Hower, both the Pt sputtering and the RIE process may induce damage due to high-energetic ion bombardment and electric fields.

2. EXPERIMENTAL

PZT sol-gel precursor was made from leadacetate-trihydrate, zirconiumpropoxide and titaniumpropoxide dissolved in buthoxyethanol. $PbZr_{.20}Ti_{.80}O_3$ thin films were deposited by spin-coating of 3 layers. After each layer, a drying (200°C, 2min, in air) and a pyrolyis step (400°C, 2min, in air) were performed, followed by a final crystallization anneal (600°C, 30min, in air). The total film thickness is 200nm. The substrates are oxidized Si wafers with Pt/Ti bottom electrode. X-ray diffraction analysis revealed pure perovskite crystalline phase and a highly-preferential (111) oriented film. Sputtered Pt was used as the top electrode, which was patterned by RIE etching using Ar gas.

The effects of different anneal conditions (pre- and post RIE) and anneal temperatures were investigated. These thermal anneals were performed in air or O_2 ambient.

The ferroelectric properties of the different samples were investigated by the P-E hysteresis loops measured in a modified Sawyer-Tower circuit, using 1kHz sinus signals with different voltage amplitudes.

3. AS-FABRICATED HYSTERESIS CHARACTERISTICS

Directly after the RIE patterning, we obtain a deformed loop which is shifted over the horizontal field axis, see Fig.1. This indicates the existence of an internal field E_i, given by the difference between the negative and positive coercive fields = $|E_c^-| - E_c^+$.

4. EFFECTS OF POST-RIE THERMAL ANNEAL

Annealing the ferroelectic capacitor after the RIE of the top electrode, changes the form of the hysteresis loop, see Fig.2a and b. A medium temperature anneal (400°C) results

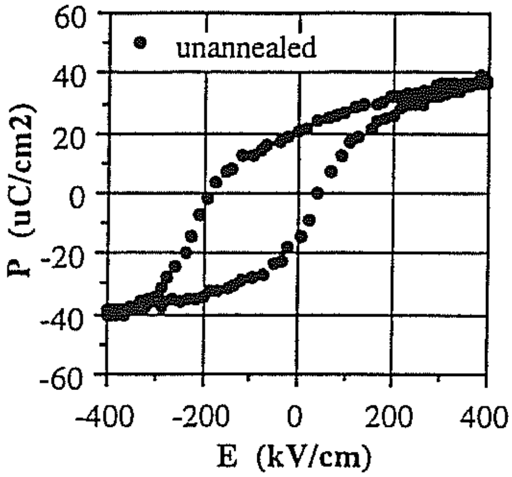

FIG. 1 : Hysteresis loop after RIE etching

in a slanted and constricted loop ("peanut"-shape), while high quality rectangular loops with maximum P_r are obtained after 600-700°C anneals.

5. SPUTTERING VERSUS RIE INDUCED-DAMAGE

To possibly distinguish between the damage introduced by the sputtering process and by the RIE process, some additional experiments were performed.

In a first experiment, the Pt top electrode was sputter-deposited through a shadow mask. This sample thus contains only the sputter damage. The hysteresis measurement shows a slanted and constricted "peanut"-shaped loop (see Fig.3a), as also obtained after the 400°C anneal of the RIE etched sample (Fig.2a).

On a second sample, a 600°C pre-RIE anneal (i.e. immedialty after the Pt sputter deposition but before the etching) was performed. As the 600°C anneal will restore the sputter-induced damage, only the RIE damage effect will be evaluated. A rectangular loop with high P_r value is obtained, however with a small horizontal field shift, Fig.3b.

Comparing with the hysteresis loop obtained after RIE without anneal, we can make the following observations :

- the Pt sputtering process has a large effect on the hysteresis loop

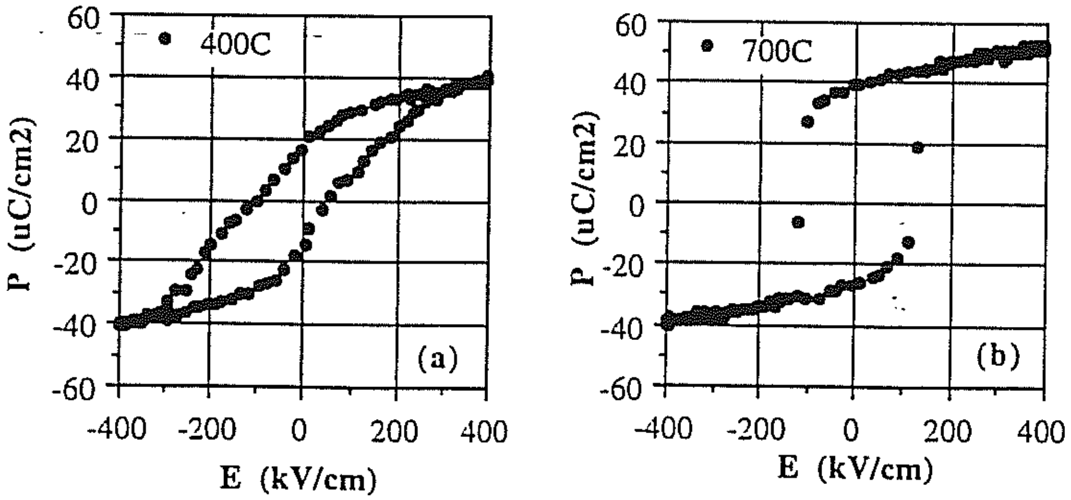

FIG.2 : Hysteresis loops after (a) 400°C and (b) 700°C post-RIE anneal.

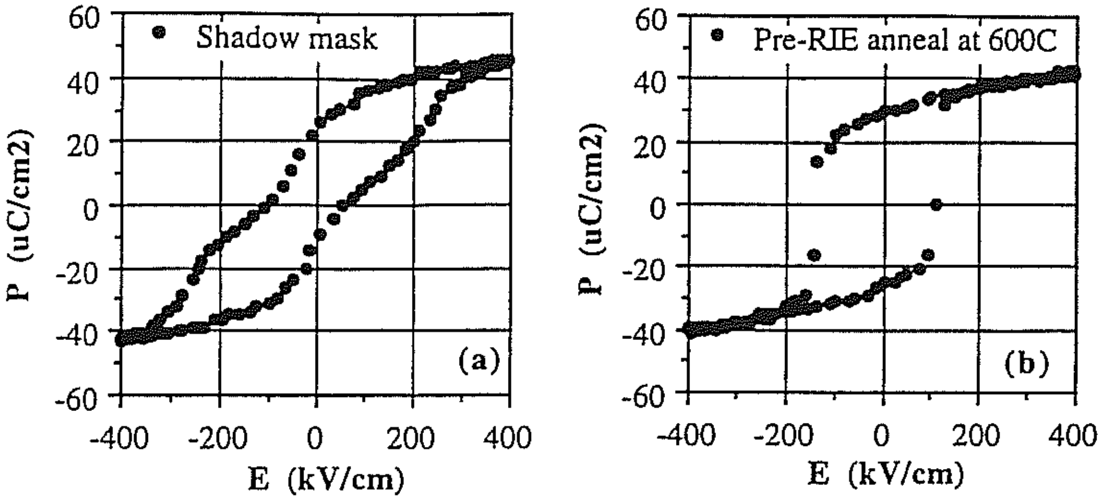

FIG.3 : Hysteresis loop of sample with (a) Pt-sputtering through shadow mask, and (b) a 600°C pre-RIE anneal.

- the RIE process has only a small effect on the hysteresis loop, except when sputter damage is already present (combined effect).

6. A DAMAGE MODEL

The starting point of our damage model is the "peanut"-shaped hysteresis loop as shown in Fig.3a. for a sample with only sputter-damage. We indeed can decompose this loop in two nearly equal-sized sub-loops, each shifted in opposite field directions (Fig.4). Similar double-loop characteristics are indeed observed in neutron-irradiated single-crystal $BaTiO_3$ by Lefkowitz et al. and in X-ray irradiated TGS materials by Chynoweth [Jona1].

We thus can observe that, except for the effect of loop slanting after sputtering, and which can be explained by the formation of a defective, non-ferroelectric interface, both sputtering and RIE result in field shifts of the hysteresis loop. In the case of sputtering, however, we have the splitting of the loops in two sub-loops; while after RIE single-loop behavior is observed.

This difference can be attributed to the poling state of the material and the mechanism of internal field creation. During the sputtering process, ionic defects may be generated and trapped at the interface of the ferroelectric film and the defective top layer, and so create internal fields. The charge sign will hereby depend on the direction of the ferroelectric polarization, and the local internal field will tend to stabilize the polarization direction, analogous to the "imprint" effect in these ferroelectric capacitors [Warren1]. In addition to the role of created ionic defects, also sample heating during the sputtering (or RIE) process may be responsible for the internal field creation, by enhancing charge injection and transport and by alignment of internal defect dipoles in the material. These "imprint"-type processes are indeed known to be very effective in highly-tetragonal PZT as used in our work.

After the PZT crystallization, there is no electrical poling of the film and, roughly, 50% of P is directed "up" and 50% "down". As a result, 50% of the material will be shifted towards negative fields, and 50% towards positive fields, which explains the double-loop behavior after the sputtering. During RIE, apparantly a high electric field is present over the sample which poles the polarization state of the film in only one direction. The resulting field shift will thus be unidirectional and single-loop behavior is maintained. The combined RIE-after-sputtering effect can be understood as the peanut shaped loop results in less effective poling as the switching fields are increased.

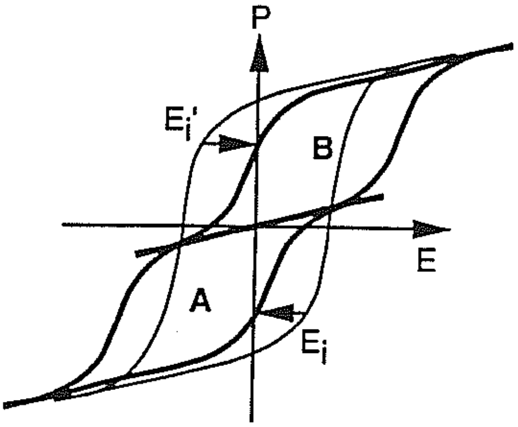

FIG.4 : Double-loop model of the "peanut"-shaped hysteresis loop after Pt-sputtering.

Hence some part of the material remains in the inverted polarization stage and double-loop behavior remains, although with a strong inequality of the sub-loops.

The effects of the thermal anneal can be explained as follows :

- a 400°C anneal removes the RIE damage but the sputter damage remains : the RIE induced field creation process apparantly is less effective (cfr. limited field shift) and is less temperature-stable than that during sputtering.
- A high temperature anneal will restore the defective interface (and improve loop rectangularity), and, as T>Tc, depoling and annihilation of existing defect dipoles will result (as P=0 in the paraelectric phase).

7. CONCLUSIONS

Both sputtering and RIE cause deformation of the P-E hysteresis loop. Sputtering results in slanted loops (by generation of defective interface) and double-loop behavior (by imprint effect). RIE poles the material and induces weak imprint.

High temperature annealing (600-700°C) results in high-quality, rectangular hysteresis loops.

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FACTORS DETERMINING THE PROPERTIES OF SOL-GEL-PROCESSED MODIFIED LEAD TITANATE THIN FILM

M.L. Calzada, M.J. Martín and J. Mendiola

Inst. Ciencia de Materiales de Madrid. 28049-Cantoblanco, Madrid (Spain)

Introduction

Modified lead titanate compositions have been recently tested as thin films and their ferroelectric, piezoelectric and pyroelectric properties have been proven to be interesting for such applications, if they are prepared in the perovskite structure (1).

The engineering of thin film devices is governed by the properties of the ferroelectric material. These properties are controlled by the material structure from the device scale down to the atomic scale. Composition influences material structure on all scales being more important in smaller structures. Many reseachers have shown how composition influences microstructrue through the formation of second phases and defects (2). Understanding of the relation among composition, crystallographic structure and microstructure becomes critical for the preparation of Pb-based perovskite films with improved electrical properties.

In this work, we discuss the preparation of sol-gel-derived modified lead titanate thin films underlaining the effect of lead oxide excesses contained in precursor solutions and heating rate of crystallization thermal treatment.

Experimental

Solutions of calcium modified lead titanate of nominal composition $Pb_{0.76}Ca_{0.24}TiO_3$ and containing different PbO excesses were synthesized by a sol-gel method described elsewhere (3). These solutions were deposited on $Pt/TiO_2/SiO_2/Si$ substrates by spin-coating. The as-deposited amorphous layers were crystallized with conventional treatments and with rapid thermal annealings.

Crystalline phases developed in the films after heating were analyzed by grazing X-ray diffraction (GIXRD).

Scanning electron microscopy (SEM) was used to study film microstructure. Thus, a thickness of $\approx 0.5 \mu m$ was measured on cross-sectioned films and an average grain size <100 nm was observed on film surfaces.

Stoichiometry of the polycrystalline films was evaluated by Rutherford Backscattering Spectroscopy (RBS).

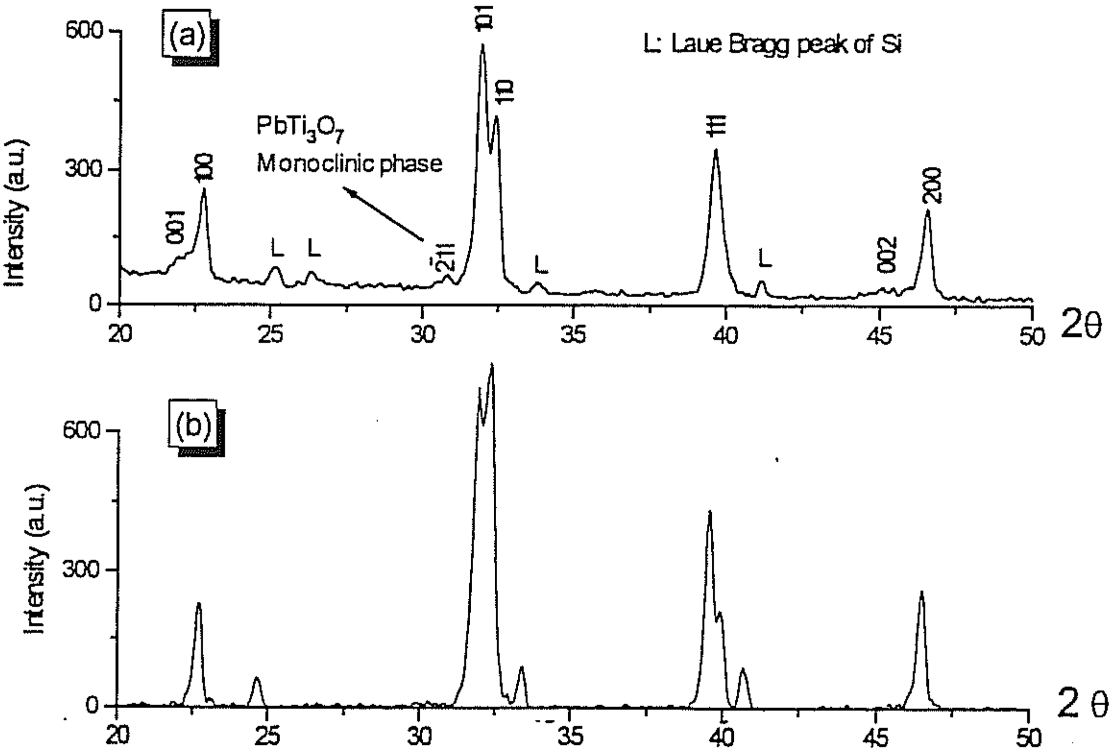


Fig.1: X-ray diffraction patterns of a) conventionally treated and b) rapid treated films.

Polarization-electric field (P-E) response was obtained in the films using a modified Sawyer-Tower circuit and applying a sinusoidal signal of 320 kV/cm amplitude at distinct frequencies, after thermal and electrical pretreatments of the samples. An overview of the ferroelectric properties of these films is detailed in another paper of this meeting (4).

Results and Discussion

GIXRD patterns of the conventionally and rapid heated films (Fig.1) indicate that in both cases the perovskite structure is formed. However, in the former an extra peak is recorded which corresponds to a lead-deficient phase. The variation in the distinct samples of this phase as a function of heating rate can be observed in fig.2. These results show how this second phase disappears in films prepared with rapid annealings. However, stoichiometry is not

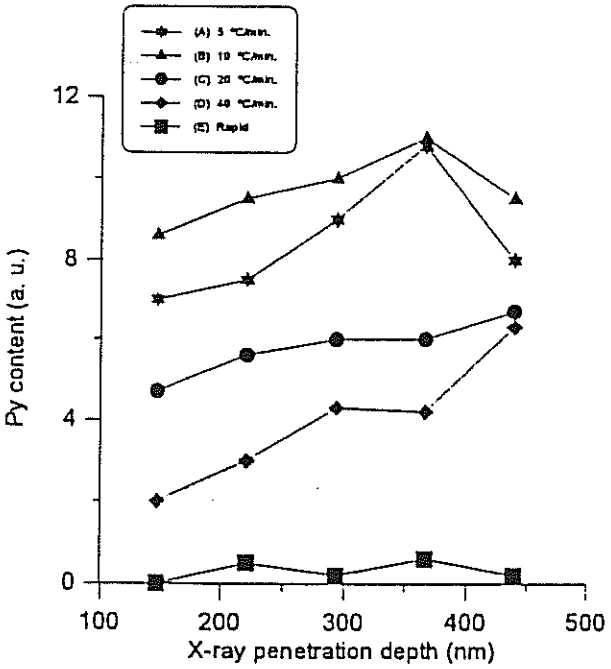


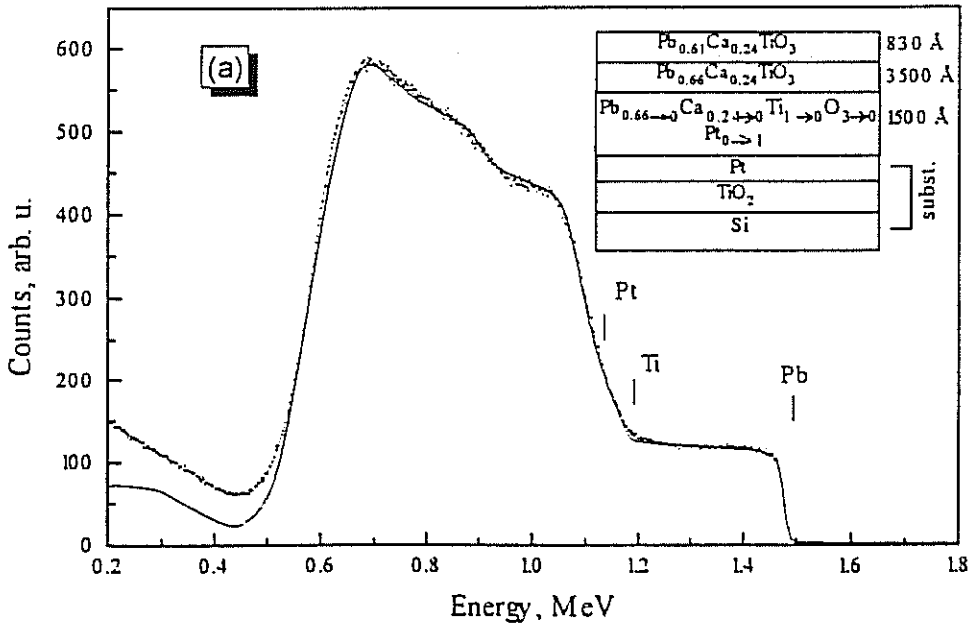
Fig.2: Variantion of PbTi3O7 content as a function of heating rate of crystallization treatment.

maintained in these films. Their composition, as evaluated from the RBS data, shows a lead deficiency not only in the bulk layer but also on the top surface of the films (Fig.3a). Also, reaction between the platinum bottom electrode and the ferroelectric layer is observed. To counterbalance this lead loss, even in rapid thermally treated samples, films were deposited from solutions containing lead oxide excesses. Fig.3b depicts the composition evaluated by RBS for modified lead titanate thin films deposited from solutions containing a 10 mole% excess of PbO and rapid thermally treated. Note that the bulk film is almost stoichiometric, however the bottom electrode - ferroelectric layer reaction is also observed in these films and an accumulation of lead is measured on the top surface of the films. Similar results have been obtained for films containing less PbO excesses.

In spite of the difficulty to obtain totally stoichiometric modified lead titanate thin films, it is observed an improvement in their ferroelectric response by incorporating excesses of lead in the precursor solutions and by using rapid annealings for crystallization.

Conclusions

Optimized sol-gel-derived modified lead titanate thin films can be prepared by using an appropriate combination of two distinct parameters: a) the content of the PbO excess of the precursor solution and b) the heating rate of the crystallization thermal treatment.



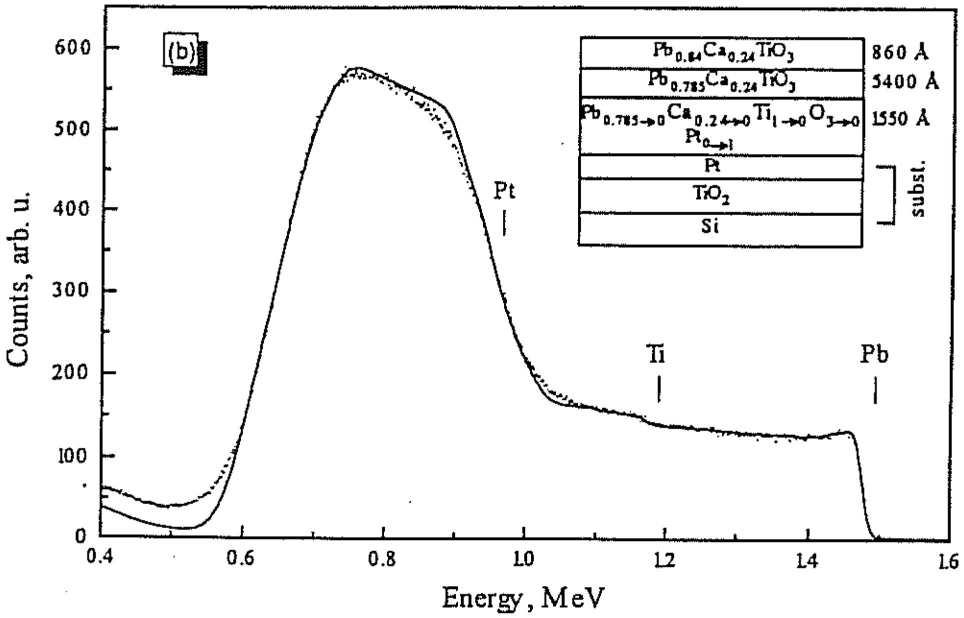


Fig.3: RBS data of a) conventionally treated and b) rapid treated films.

However, the obtention of completly homogeneous lead titanate perovskite thin films is quite difficult due to the special physico-chemical characteristics of the lead titanate system and to the anisotropic nature of thin films.

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Acknowledgments

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PRECURSOR CHEMISTRY AND PROPERTIES OF SOL-GEL PZT THIN FILMS

M. Kosec, U. Delalut, B. Malič, and G. Dražič
Jožef Stefan Institute, University of Ljubljana, Jamova 39, 1001 Ljubljana, Slovenia

Abstract - Sol-gel derived $Pb(Zr_{0.53}Ti_{0.47})O_3$ films were prepared by spin coating on platinum coated silicon wafers. Sol for deposition was prepared from Zr and Ti alkoxides and different lead precursors - standard lead acetate hydrate and a new lead oxide based precursor. Crystallisation, microstructure and hysteresis properties of these films were studied and compared in order to reveal the feature of the two synthesis methods employed.

1: Introduction

Among different techniques employed for the preparation of ferroelectric thin films, the sol-gel route in addition to low capital cost, offers the possibility of retaining the purity and the chemical homogeneity from the starting sol to the final film.

To obtain the chemical homogeneity of a multicomponent crystalline film, precursor containing the metal ions in stoichiometry, that is required in final product, needs to be synthesised. Complex precursor has to be characterised by the low reactivity towards water to avoid fast hydrolysis and consequent precipitation, of proper viscosity, good wettability and long term stability.

Lead acetate and simple alkoxides of Ti and Zr in methoxyethanol is presumably the most widely used precursor system in sol-gel processing of PZT films. The synthesis of complex Pb-Ti-Zr- precursor is characterised by the variety of chemical reactions (1,2) yealding in a mixture of species with pure defined chemical composition and structure rather than compound with perovskite stoichiometry. The chemical homogeneity is improved by long reaction time (3) and extensive solvent exchange (4) that reflects in improved ferroelectric properties.

Another approach is to change the precursor system. From the point of view of ligand chemistry Pb-alkoxide would be better choice as compared to Pb-acetate.

As reported alkoxide of nonmetallic elements can be synthesised from oxides (5). Since lead has weak metal character we assumed that lead oxide might be used for synthesis of akoxides.

In this paper we briefly compare crystallisation, microstructure and hysteresis properties of sol-gel PZT 53/47 thin films derived from lead acetate and lead oxide, respectively.

2. Experimental work

The synthesis of Pb-Zr-Ti complex solution was performed in a dry argon atmosphere by dissolving anhydrous lead acetate or by dissolving lead oxide in the solution of Ti and Zr n-propoxides in 2-methoxyethanol solvent. 10 mole % of PbO excess was used. Subsequently the solution was refluxed for 2 hours and distilled to achieve the concentration of approximately 0.5 M. After cooling to room temperature 4 vol. % of formamide was added to the solution. The chemicals used were reagent grade. Solid content of the metal compounds was determined gravimetrically.

The films prepared from lead acetate based sol and lead oxide based sol were deposited on the Pt/Ti/SiO_2/Si wafers at 3000 rpm for one minute and then pyrolysed at 350°C for one minute. Deposition procedure was repeated for five times to obtain thicker films. Films were put in a furnace at temperatures between 500-700°C and annealed for different period of times. They were also heated at a rate of 10°C/min to 700°C.

XRD, SEM and TEM analyses were performed and hysteresis loops were measured on prepared films.

3. Results and discussion

According to XRD analysis after pyrolysis at 350°C, PZT films consist of amorphous matrix and pyrochlore. After firing at temperatures between 600-700°C, formation of the perovskite phase can be observed. Complete transformation to the perovskite structure can be obtained by firing the PZT films at 700°C for 5 min. Results of the XRD analysis of PZT films reveal that the perovskite structure can be obtained by using either lead acetate or lead oxide as precursor and that the heating rate has no significant influence on phase evolution in thin films. However, the SEM analysis of the PZT films revealed differences in microstructures and phase compositions of the films, prepared from lead oxide or lead acetate and fired under different heating regimes (Fig. 1).

Although pyrochlore phase can not be observed in the XRD patterns, we can still observe residual pyrochlore phase among perovskite grains in PZT films prepared from lead acetate. Firing of PZT thin films, prepared from lead acetate, either by putting a film in a 700°C hot furnace or by heating at a heating rate of 10°C/min produces similar microstructures. However, rapid heating results in a finer texture of the film. Microstructures of PZT thin films prepared from lead oxide are very fine grained with submicrometer grains. We can observe a strong effect of the heating rate on microstructural development. It is obvious that firing of the films by putting them in a hot furnace produces homogeneous microstructure, whereas in the case of firing at a heating rate of 10°C/min results in less homogenous microstructure with microcrystalline surface pyrochlore. No surface pyrochlore can be observed by SEM at rapid annealed films from PbO.

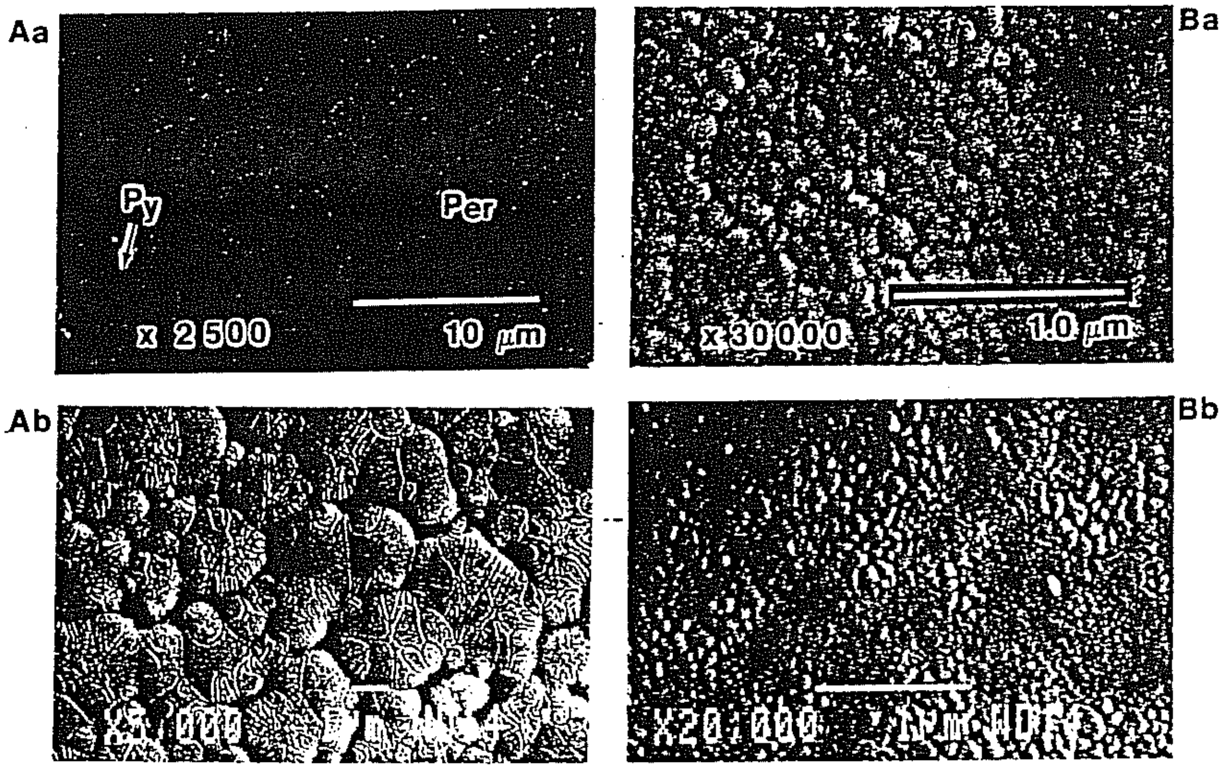

Fig. 1: SEM micrographs of the 53/47 PZT films prepared from A: $Pb(OAc)_2$ or B: PbO. Films were fired by a: rapid annealing (700°C, 20 min.) or b: by heating at a rate of 10°C/min to 700°C, 20 min.

Results of the TEM analysis confirm that there is no detectable amount of pyrochlore phase in rapidly annealed lead oxide based PZT film. We do observe residual pyrochlore phase in lead acetate based PZT film, treated under the same thermal conditions.

The results can be qualitatively explained by the high energy of nucleation of lead acetate based PZT films and therefore number of nuclei is small. Once the nuclei are formed they grow fast because the energy for grain growth is lower than the energy of nucleation (6). The nucleation proceeds even after the first nuclei begin to grow, therefore we have two competing processes: nucleation and growth. They result in inhomogeneous microstructure with a wide grain size distribution (7). Furthermore heterogeneous nucleation on the Pt electrodes was reported as predominant nucleation mechanism (6). Under these conditions one can expect the grain thickness is equal to film thickness. By using lead oxide as the lead precursor, we lower the energy of nucleation and the number of nuclei at the first stage of nucleation is much higher than in the lead acetate based system. When nuclei start to grow, they will soon meet their growing neighbours and therefore grain growth is inhibited - developed microstructure has submicron grain sizes and a narrow grain size distribution. Further study is needed to explain the absence of pyrochlore in lead oxide derived PZT films.

Different microstructure of films results in different hysteresion properties.

Rapidly heated up and annealed at 700°C, 20 min. lead acetate based PZT film exhibit P_r 8 $\mu C/cm^2$ at coercive filed 25 kV/cm while lead oxide based PZT film shows 12 $\mu C/cm^2$ and E_c 90 kV/cm.

4. Conclusions

Lead oxide is used as a precursor in sol-gel processing of PZT thin films. It dissolves in methoxyethanol with the reaction of Zr and Ti n-propoxide. It forms stable, spinable solution. Amorphous precursor crystallises via pyrochlore to perovskite in 5 min. at 700°C. Rapid annealing of PbO based films results in fine grain microstructure with minor amount of pyrochlore whereas acetate films processed under identical conditions exhibit rosette type microstructure with residual pyrochlore. The difference in microstructure is explained by the difference in nucleation rate. PZT 53/47 PbO based films have Pr 12 $\mu C/cm^2$ and E_c 90 kV/cm.

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PREPARATION OF PZT FILMS AND POWDERS BY THE SOL-GEL PROCESS

MACİT ÖZENBAŞ
Department of Metallurgical Engineering, Middle East Technical University, Ankara, 06531 Turkey

ABSTRACT

The present paper describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

INTRODUCTION

In recent years, preparation and synthesis conditions of uniform and chemically homogeneous particles of ferroelectric ceramics have been investigated by numerous researchers using sol-gel alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely homogeneous precipitation from aqueous solutions.[1] This method involves the reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 75-98°C to produce the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia.

EXPERIMENTAL PROCEDURE

The materials required for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$, and $PbCl_2$, together with some urea. The concentrations studied are given below :

Pb^{+2}	0.001 - 0.005 M
Zr^{+4}, Ti^{+4}, Urea	0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, together with urea in sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solutions. The resulting PZT precursors were gelled by holding at 90°C for 1 to 2 h while magnetically stirring. The starting pH of the precursors was between 0 and 1. However, the pH gradually increased to 5-5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution. These precipitates were dried at 120°C for 5-6 h in an oven and then they were fired at 350°C, 650°C, and 850°C for 5, 5, and 3 h, respectively, in the oxygen atmosphere to obtain polycrystalline powders.

The substrate materials for the films are silicon (111) wafers and α-Al_2O_3. The coating of the films was accomplished by dipping the substrates into the coating solutions, which were obtained from the precursors used for the powder formation. The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analyses of the bulk gels. The coated films were dried at around 100°C for 10 min. The above process should be repeated in order to increase the thickness of the films. A film of approximately 0.2 µm thick was deposited in a single process and the final film thicknesses determined by SEM were about 1.1-1.2 µm. Finally, the films were annealed at 350°C, 650°C, and 850°C for 3 h in open alumina crucibles in the oxygen atmosphere to obtain crystallization. The heating and cooling rates used were 20°C/min and 1.5°C/min, respectively. The particle size, the morphology and the film surfaces were observed from SEM (Jeol-JSM 6400) micrographs. EDX analyses were carried out on the same samples to give information on the composition of the films.

RESULTS AND DISCUSSION

The resulting crystal structure of sol-gel derived PZT thin films was highly sensitive to both the initial chemical composition and heat treatment temperature. In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. Sol-gel derived powder samples crystallized at temperatures approximately 50°C lower than corresponding thin film samples. Consistent with the literature, the development of the initial pyrochlore phase was observed during the thermal processing of thin films. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent.[2,3] In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analyses showed that films of 1.1-1.2 µm thickness were polycrystalline with no preferred crystallographic orientation (Fig. 1).

For the observation of powders, small amounts of the suspensions were rapidly dried by heating on common SEM sample holders, the surface of which had additionally been polished to less than 0.5µm surface roughness.[4] Figure 2.a shows the particles of PZT composition obtained by using urea, which yielded particle sizes from submicron range to a few microns. The particles of the same composition obtained without the use of urea were about 50-100 µm in size (Figure 2.b). The use of the homogeneous precipitation process leads to micron-sized particles with high homogeneity and possibly gives films with better physical properties.

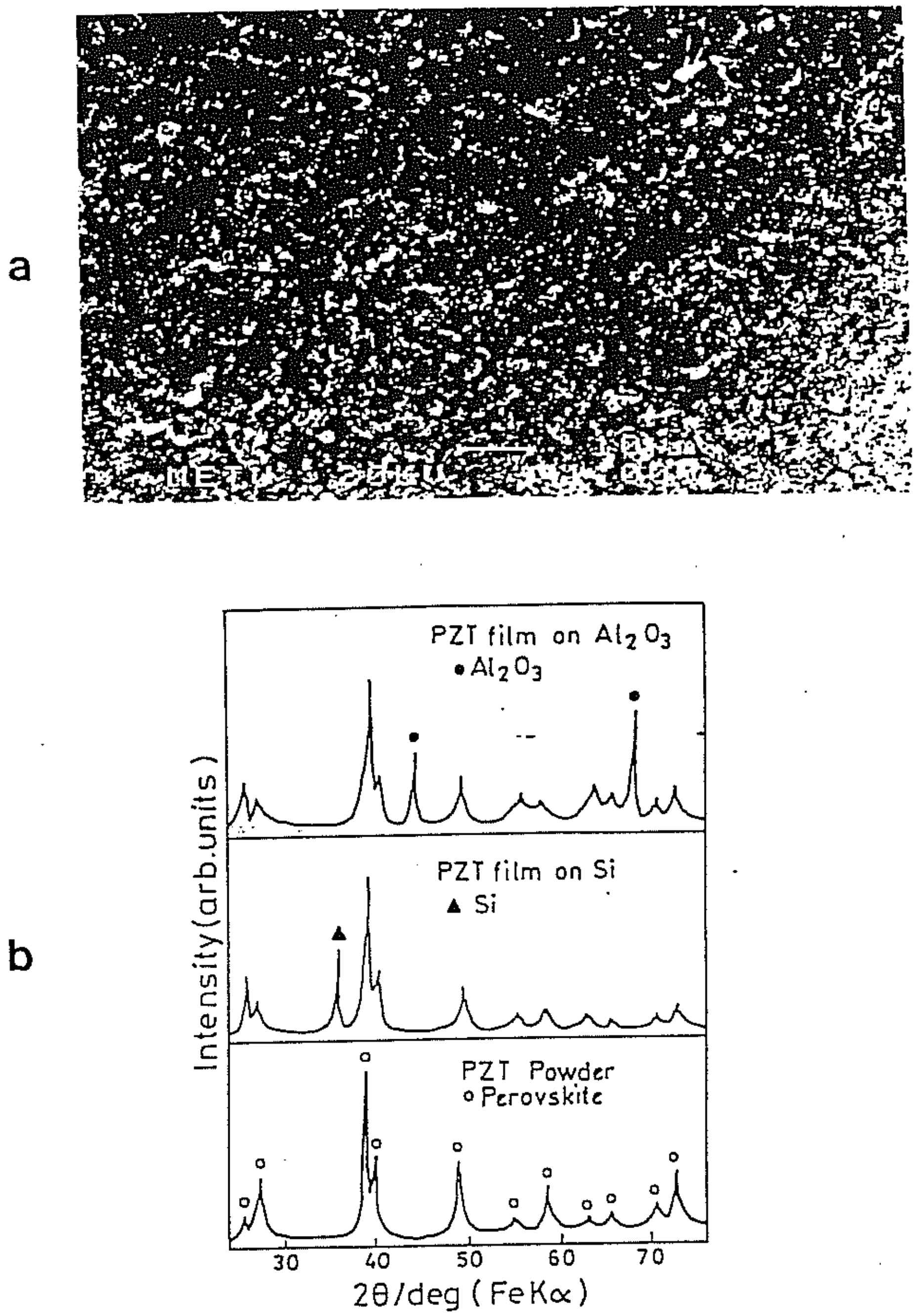

Figure 1. (a) Scanning electron micrograph of the PZT film surface on alumina substrate, heat treated at 850°C for 3 h, (b) XRD patterns of the films on alumina and silicon substrates.

Conversion of the precipitated amorphous powders to the PZT oxide phase was evaluated by X-ray diffraction. XRD studies show that the crystallization started around 350°C. Heat treatment at 650°C decreased the amount of pyrochlore phase and finally at 850°C, the sample was all perovskite phase. This temperature is especially important for lead-containing systems to avoid the PbO loss problem during heat treatment.[5] The crystal structure appeared to transform from pseudocubic to tetragonal with increasing temperature, and the original composition was slightly to the tetragonal side of the morphotrophic phase boundary.[6] The enhanced definition of tetragonal splitting, with increased intensity at higher temperatures, indicates a greater degree of crystallinity for material heat-treated at these temperatures. The lattice parameters for the gel-derived powders agree with those of the sintered samples, which indicates that the chemical composition of the gel-derived powders does not deviate much from that of the starting solutions.[7]

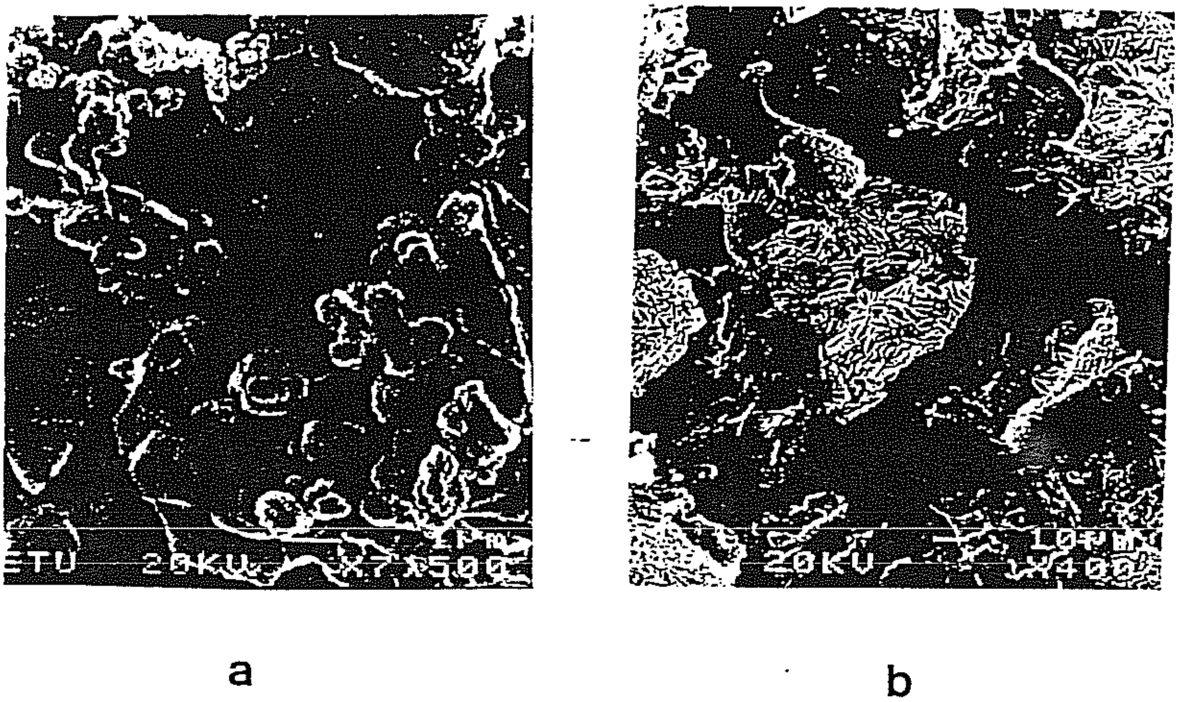

Figure 2. (a) Scanning electron micrograph of sol-gel derived PZT particles obtained by using urea, (b) Scanning electron micrograph of sol-gel derived PZT particles obtained without the use of urea.

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Barium Titanate Thin Films: Influence of Precursor Chemistry and Processing on Thin Film Properties

S. Hoffmann, U. Hasenkox and R. Waser

Institut für Werkstoffe der Elektrotechnik (IWE)
RWTH Aachen University of Technology, Germany

Abstract

Polycrystalline barium titanate thin films were prepared by chemical solution deposition (CSD) on platinum coated silicon substrates. The influence of precursor chemistry and processing on the morphology and electrical properties of the thin films was investigated by IR spectroscopy, X-ray diffraction analysis, scanning and transmission electron microscopy and impedance analysis.

Introduction

Dielectric thin films of $BaTiO_3$ and $(Ba,Sr)TiO_3$ are widely investigated for thin film integrated capacitors and storage capacitors in DRAM-applications. The films were deposited by sputtering, chemical vapor deposition (CVD), laser ablation, and chemical solution deposition (CSD). $BaTiO_3$ thin films, which were deposited on platinum coated silicon substrates at temperatures below 750°C are polycrystalline and exhibit a pseudocubic structure[1-10]. Epitaxial $BaTiO_3$ thin films grown by pulsed laser deposition on (001) oriented single crystals show a ferroelectric hysteresis with a remanent polarization of 4.0 $\mu C/cm^2$ and a coercive field of 12.5 kV/cm[14]. The fine grained $BaTiO_3$ thin films with permittivities between 100 and 800 show a super-paraelectric behaviour with a slightly negative temperature coefficient of the dielectric constant in the region between room temperature and 250°C[2,7,16]. No tetragonal distortion of the unit cell could be detected by X-ray analysis and therefore no phase transition from the cubic to the tetragonal phase could be observed, in contrast to what is known from bulk ceramics[11]. This fact could be attributed to the small grain size in the thin films. Uchino[12] reported, that the critical grain size of sputtered $BaTiO_3$ thin films, for which a clear separation of cubic and tetragonal phase is still possible, is in the range of 100 and 200 nm.

The permittivity of the polycrystalline thin films depends on the porosity and the grain size[11,12]. The grain size dependence of the dielectric properties of $BaTiO_3$ thin films makes it necessary to achieve an understanding of the correlation between processing, morphology, and electrical properties. In the following study of the influence of precursor chemistry and processing on the morphological and dielectric properties of $BaTiO_3$ thin films we discuss a few aspects of the above mentioned correlation.

Experimental procedure

Polycrystalline $BaTiO_3$ thin films were deposited on platinum coated silicon wafers. Different precursor solutions as well as different heating procedures were used. The structure of the films was analyzed by glancing angle X-ray diffraction on a Philips Thin Film System. The morphology of the films was studied by scanning electron microscopy on a ZEISS FE-SEM Gemini 986 and by transmission electron microscopy and HR-TEM[15]. For contacting the platinum bottom electrode a part of the film was etched by means of photolithography. At the sharp edge the film thickness was measured with a DEKTAK profilometer. Electrical measurements were performed on Pt / $BaTiO_3$ / NiCr-Au configurations using a HP4275 multi-frequency LCR bridge with a 10kHz signal.

Results and Discussion

In the following we discuss steps of the CSD-process, which are relevant for the microstructure of the thin films. These are the barium and titanium precursor chemistry, the concentration of the spin-on solution and the heating procedure.

Figure 1 shows the flow diagram of the process. As Ba-precursors we used different carboxylates, starting with the acetate and ending with the 2-ethylhexanoate.

The investigated Ti-precursors were pure titanium butylate and $Ti(OBu)_4$ stabilized with 2 mols acatylacetone.

The molarity of acetate and propionate based solutions was varied between 0.2 molar and 0.5 molar. The effect on the thin film properties was studied by SEM and impedance analysis.

In the standard heating procedure each coating was heated at 750°C and the whole film was annealed at 750°C or 800°C.

In the crystallization study each coating was pyrolyzed at 450°C and the whole film was sintered at temperatures between 550°C and 800°C. The crystal structure of the films was analysed by X-ray diffraction.

Table 1 lists the morphological and electrical properties of the $BaTiO_3$ thin films, which are derived from the different Ba-/Ti-precursors.

Figure 2 shows the temperature dependence of the permittivity of $BaTiO_3$ thin films derived from differently concentrated solutions.

Figure 3 shows the X-ray diffraction diagram of the crystallization study of the $BaTiO_3$ thin film grown from the amorphous phase.

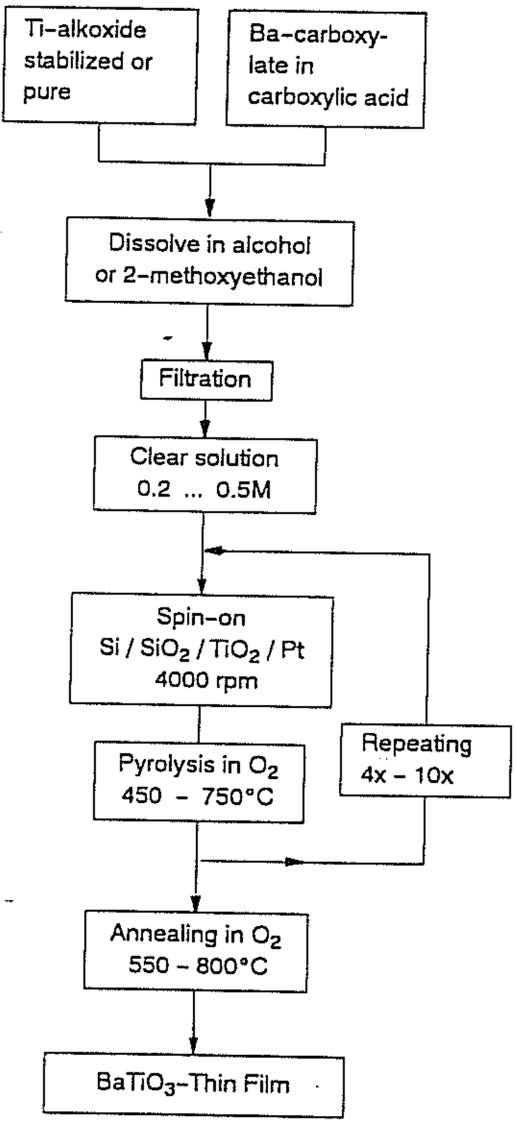

Fig. 1: CSD-processing of $BaTiO_3$ Thin Films

Precursors	Grain size (nm)	Thickness (nm)	Permittivity at 10kHz, 25°C	Dissipation factor at 10kHz, 25°C
Ba-Acetate Ti-Butylate	40 - 170	255	516 ± 7	0.041
Ba-Propionate stab. Ti-Butylate	40 - 180	215	650 ± 20	0.076
Ba-Propionate Ti-Butylate	40 - 150	250	540 ± 15	0.052
Ba-2-Methylpropionate Ti-Butylate	40 - 100	245	507 ± 22	0.066
Ba-2-Ethylhexanoate Ti-Butylate	40 - 80	100	344 ± 7	0.060

Tab. 1: Morphological and electrical properties of $BaTiO_3$ *thin films from different precursors heated at 750 °C* [16,17]

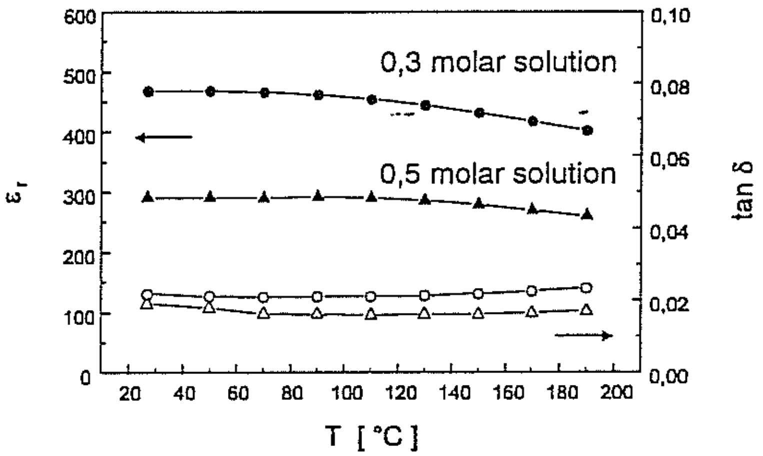

Fig. 2: Permittivity ε_r *and dissipation factor tanδ of* $BaTiO_3$*-thin films as a function of the temperature and the concentration of the acetate-based spin-on solution* [17]

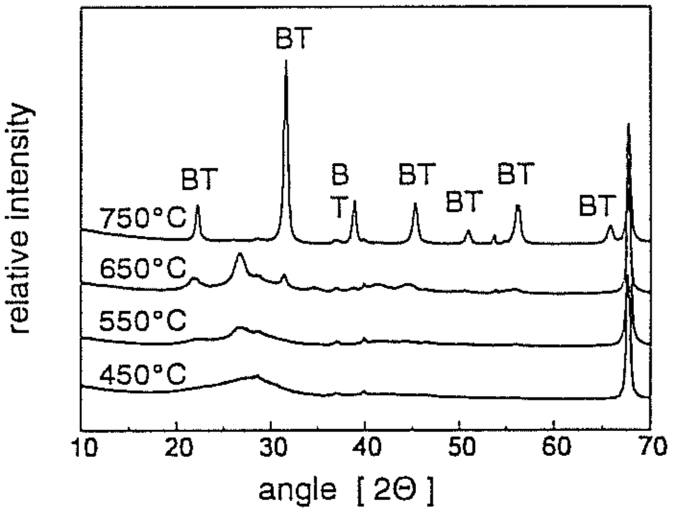

Fig. 3: X-ray diffraction diagrams showing the crystallization in $BaTiO_3$ *thin films from the amorphous phase (450°C)*[16]

Summary

- $BaTiO_3$ thin films were prepared by chemical solution deposition (CSD) on platinum coated silicon substrates.
- XRD analysis of films heated at temperatures > 700°C reveals a pseudocubic perovskite structure without any detectable amount of second phase.
- Different Ba-carboxylate precursors were used. The Ba-carboxylates with short alkyl chains decompose at higher temperatures than the 2-ethylhexanoates, which was investigated by IR-spectroscopy.
- SEM analysis shows that the films derived from carboxylates with long alkyl chains consist of smaller grains than the films which are derived from Ba-acetates or -propionates. This is in agreement with the lower permittivity which was measured for the $BaTiO_3$ films derived from the 2-ethylhexanoate precursor.
- The effect of a monomeric or oligomeric Ti-compound was investigated for solutions of pure titanium alkoxide precursors versus stabilizied Ti-alkoxides. Films derived from stabilized alkoxides exhibit strongly agglomerated grains which result in a higher dielectric constant compared to the films from the pure Ti-alkoxide.
- Dense $BaTiO_3$ thin films with grain sizes in the range of 60 nm and high dielectric constants were obtained from spin-on solutions with concentrations up to 0.3 molar. Films grown from a 0.5 molar solution exhibit a higher porosity and a lower dielectric constant.
- Crystallization studies show, that films derived from Ba-acetate or -propionate precursors crystallize via an intermediate phase, which is stable between 550°C and 650°C.
- Pyrolysis of each coating at a temperature of 450°C and sintering of the whole film at 750°C results in a fine grained $BaTiO_3$ thin film with low permittivity compared to films heated at 750°C.
- All the $BaTiO_3$ thin films show a slightly negative temperature coefficient of the permittivity. None of the films show a P(E)-hysteresis.

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Pulsed laser deposition and electrical characterization of Ca-modified lead titanate thin films

C. Zaldo, M. J. Martín and J. Mendiola

Instituto de Ciencia de Materiales de Madrid. CSIC.
Campus Universitario de Cantoblanco. 28049 Madrid. Spain.
email: cezaldo@ccuam3.sdi.uam.es

Pulsed laser deposition technique has been used to prepare $Pb_{1-x}Ca_xTiO_3$ thin films on $Pt/TiO_2/SiO_2/(100)Si$, (100)MgO, YBCO/(100)MgO and $(100)SrTiO_3$ substrates. The composition, crystalline quality and morphology of the films obtained have been characterized. Films with thickness above 500 nm show an electrical resistance larger than 1 MΩ. Ferroelectric behavior has been observed in films deposited on $Pt/TiO_2/SiO_2/(100)Si$. After electrical treatment the remanent polarization of the films reaches values above 1 $\mu C/cm^2$ for 20 V of applied voltage.

Introduction

The incorporation of Ca to $PbTiO_3$ reduces the lattice tetragonality (c/a) [1] yielding films resistant to cracking upon cooling from the deposition temperature (cubic phase) to room temperature (tetragonal phase) [2]. Moreover, other physical material properties are modified, namely: *i)* The Curie temperature (T_c) decreases with increasing Ca concentration. This yields an increase of the room temperature pyroelectric coefficient [2]. *ii)* The ratio of the transversal and in-plane piezoelectric coupling coefficients (K_t/K_p) is minimized at about 24% of molar Ca concentration [3].

Thin films of $Pb_{1-x}Ca_xTiO_3$ (hereafter PCaT) have been previously prepared by radio frequency magnetron sputtering [2] and by sol-gel processing [4]. The purpose of the present work is to determine the experimental conditions required to produce PCaT films by pulsed laser deposition (PLD) technique and to characterize their physical properties with emphasis in the electrical response.

PLD technique was selected to prepare Ca-modified ferroelectric $PbTiO_3$ films because it has been successfully used to prepare highly oriented films of $PbTiO_3$ and its alloys with Zr and La [5].

Experimental technique

We have used sintered $Pb_{0.76}Ca_{0.24}TiO_3$ ceramic targets 10 % weight PbO-rich. The sintering method of the pellets has been described previously [6]. Also pressed targets were prepared for comparison purposes. To prepare these targets a mixture of PbO, TiO_2 and $CaCO_3$ powders was heated at 600° C to eliminate carbon, pressed uniaxially at 300 kg/cm^2, isostatically at 2000 kg/cm^2 and finally dried at 600° C. The target composition was measured by x-ray fluorescence analysis and used to calibrate the EDX measurements of thin films.

Figure 1 shows an schematic view of the deposition technique. A KrF laser beam (248 nm, 300 mJ/ pulse, 20 ns) is focused onto the target at 45°. The target is rotated in a turbo pumped chamber at 20 rpm. The induced plasma expands in a dynamic low pressure (10^{-6}-10^{-1}mbar) oxygen atmosphere and the film is deposited on a heated substrate placed parallel to the target. The substrate may be heated up to 700° C. A thermocouple is used to monitor the substrate temperature.

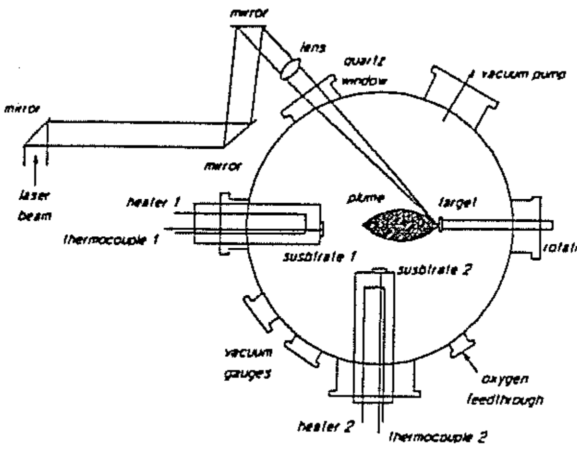


Figure 1. Deposition chamber

$Pt/TiO_2/SiO_2/(100)Si$ wafers were usually used for substrate. Also some tentative depositions has been performed on (100)MgO, YBCO/ (100)MgO and (100) $SrTiO_3$ crystals.

The average thickness of the films has been determined using a mechanical stylus. The composition of the films formed has been measured by energy dispersive x-ray (EDX) analyses and by Rutherford Back-Scattering (RBS) technique. The morphology by electron scanning and atomic force microscopies. The crystallinity has been studied by grazing angle and Θ-2Θ x-ray diffraction.

Sputtered Pt dots are used as top electrode. The electrical characterization of the hysteresis behavior has been performed at room temperature with an standardized ferroelectric test system using a modified Sawyer Tower circuit.

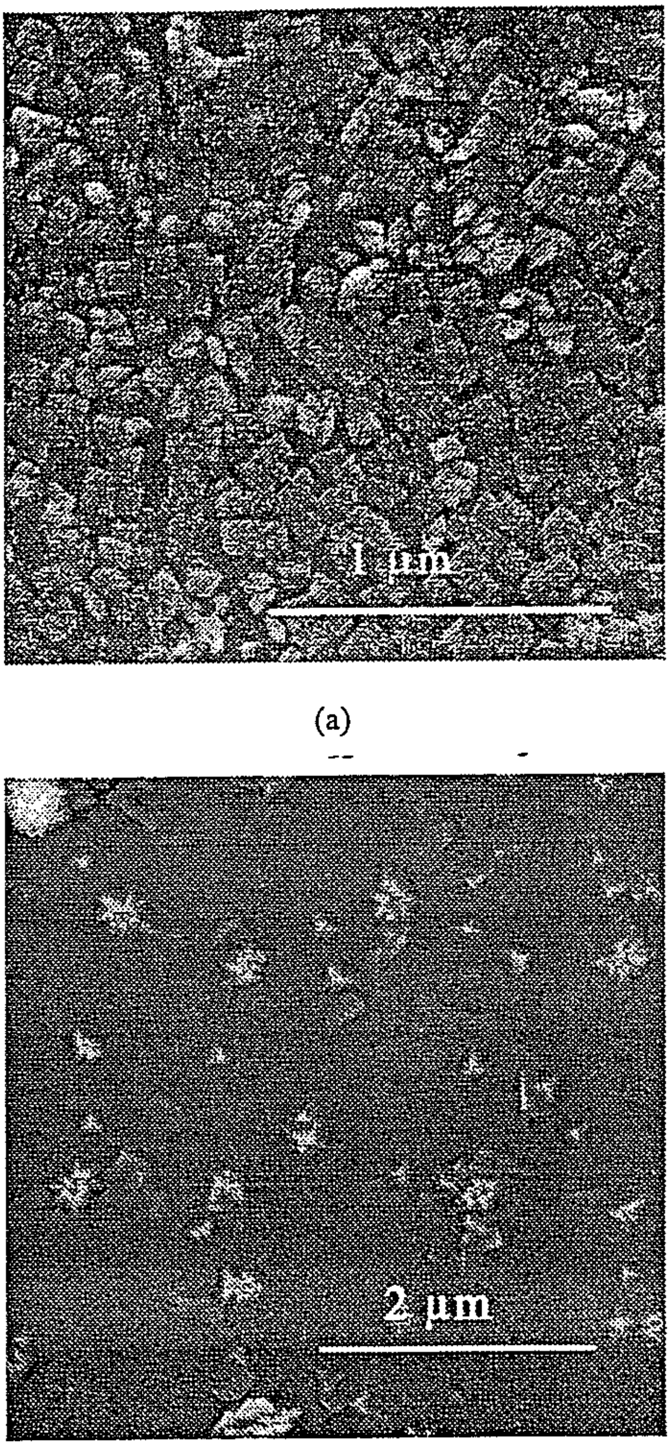
Experimental results

The threshold laser fluence (J_o) of the sintered and pressed targets have been determined from the film deposition rate. For the two types of targets used the ablation threshold was J_o= 1.5 J/cm^2. Little differences have been found in the crystal quality of the films formed using sintered or pressed targets. The most significant difference is that films prepared using sintered targets have a lower density of undesired particles. Increasing the laser fluence (J) up to 11 J/cm^2 we have found only small differences in the [Ca]/[Ti] and [Pb]/[Ti] concentration of the films, however using large J produces crystalline films with improved crystallinity and orientation.

From the EDX analyses it has been concluded that [Ca]/[Ti] ratio of the film is very close to that obtained in the target and that it is little sensitive to the deposition parameters, namely, laser fluence (J), substrate-target distance (d_{st}), oxygen pressure (pO_2) and substrate temperature (T_s).

The [Pb]/[Ti] ratio obtained by EDX has been normalized to that obtained from the RBS simulation performed in some selected samples. The [Pb]/[Ti] ratio in the film is very sensitive to the deposition conditions: A slight decrease has been found for increasing J and a slight increase has been found for increasing d_{st} but the two most important parameters to control the Pb concentration in the film are pO_2 and T_s. In agreement with previous observations in other $PbTiO_3$-based films prepared by PLD [5], the [Pb]/[Ti] ratio markedly increases with increasing pO_2 and decreases rapidly at T_s>500° C.

In order to obtain a good thickness homogeneity across the substrate size (10x10 mm^2) the



(a)

(b)

Figure 2. $Pb_{0.76}Ca_{0.24}TiO_3$ on $Pt/TiO_2/SiO_2/(100)Si$. (a) Sample PTC285. (b) Sample PTC311.

substrate has been hold 4 cm away from the target. Films deposited on substrates heated above 45 C show crystalline PCaT perovskite phase free of contamination with no evidence of pyroclo phases.

On Pt/TiO_2/SiO_2/Si substrates, films with optimized crystallinity were obtained close to 55 C using $pO_2 = 1x10^{-1}$ mbar. The first growth steps (film thickness < 200 nm) are characterized by t presence of isolated cubes (figure 2a), these cubes are preferentially oriented with the [10 direction perpendicular to the substrate surface but are porous and not useful for electric measurements. Thicker (500-1000 nm) films show a more complex morphology which include planar regions with 30 nm of average roughness and isolated prominent features with C_3 symmetr (figure 2b), these films are also preferentially oriented as the thinner ones, but show increasin contributions of other PCaT orientations, namely [001], [101], [110] and [111]. We believe that th triangular features observed in thicker films are related to the growth of [111] oriented PCaT.

For electric waves of 1 V of amplitude, the thick PCaT films show electrical resistance in th range 10^7-10^6 Ω. Electrical measurements have been performed on these films to characterize th ferroelectric behavior. Figure 3 shows the increase of the remanent polarization (P_r) with applie voltage (V) in as-deposited samples. A further increase of P_r is achieved submitting the samples t an electrical treatment by decreasing from 10 to 0 V the amplitude of a low frequency (0.2 Hz electric wave.

In order to improve the PCaT orientation with the ferroelectric [001] axis perpendicular t the substrate further depositions are currently performed on (100)MgO, PLD deposited YBCO o (100)MgO and (100)$SrTiO_3$. The best results have been obtained on bare (100)MgO.

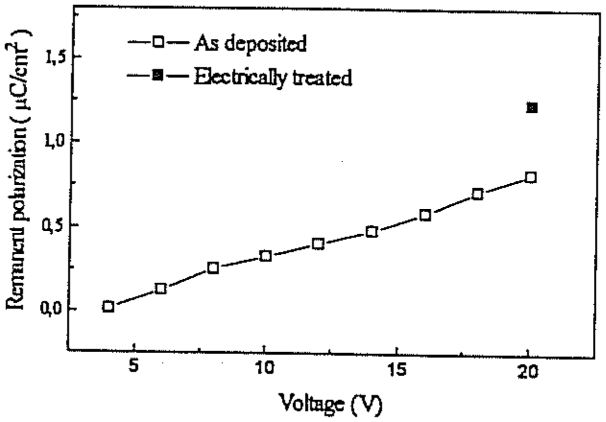


Figure 3. Remanent polarization of PLD $Pb_{1-x}Ca_xTiO_3$ films on Pt/TiO_2/SiO_2/Si substrates.

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FACTORS CONTROLLING THE PHASE DISTRIBUTION OF PZT FILMS PREPARED BY PLD

B.E. Watts[1], F. Leccabue[1], A. Diodati[1], E. Vasco[1], G. Bocelli[2], P. Mengucci[3], A. di Cristoforo[3] and A. de Benedittis[3]
[1]MASPEC/CNR Institute, Via Chiavari 18/a, I-43100 Parma, Italy
[2]CSSD/CNR Centre, Viale delle Scienze, I-43100 Parma, Italia
[3] Dipto. di Scienze dei Materiali e della Terra, Univ. di Ancona, I-60131 Ancona Italy

The most important issue during the growth of polycrystalline and epitaxial thin films of PZT is the control of the phases formation and in particular the narrow divide between crystallising perovskite and pyrochlore phases. Much of the interpretation of the phenomena observed is based on knowledge acquired on bulk sample preparation; this may differ from thin film crystallisation in several respects; the relatively large particle size produced by mechanical mixing and grinding of the oxide powders means that the reaction between lead, zirconium and titanium oxides is diffusion limited, in addition, this implies that it must be performed at high temperatures at which the lead evaporation is much higher and the phase equilibria may different from those at which thin films are made. The research carried out within the COST Project has been to determine the relative importance of factors which control the formation of the ferroelectric phase.

A pulsed laser deposition system has been developed at the Istituto Maspec/CNR and employs a XeCl excimer laser to ablate material onto heated substrates, held at a distance of 40-45mm. The system is described in detail in reference [1]. Although laser deposition has some limitations as an industrial production method, it is a valuable laboratory tool and, in this case growing films on heated substrates makes epitaxial growth possible and is comparable with other techniques such as sputtering and MOCVD.
Films were grown under a different conditions and the process parameters studied were: (i) growth temperature; (ii) substrate type; (iii) post processing; (iv) target composition.

The films were analysed by X ray diffraction and electron microscopy.

Growth Temperature.

A X ray diffraction spectra of a series of samples is shown in Figure 1.

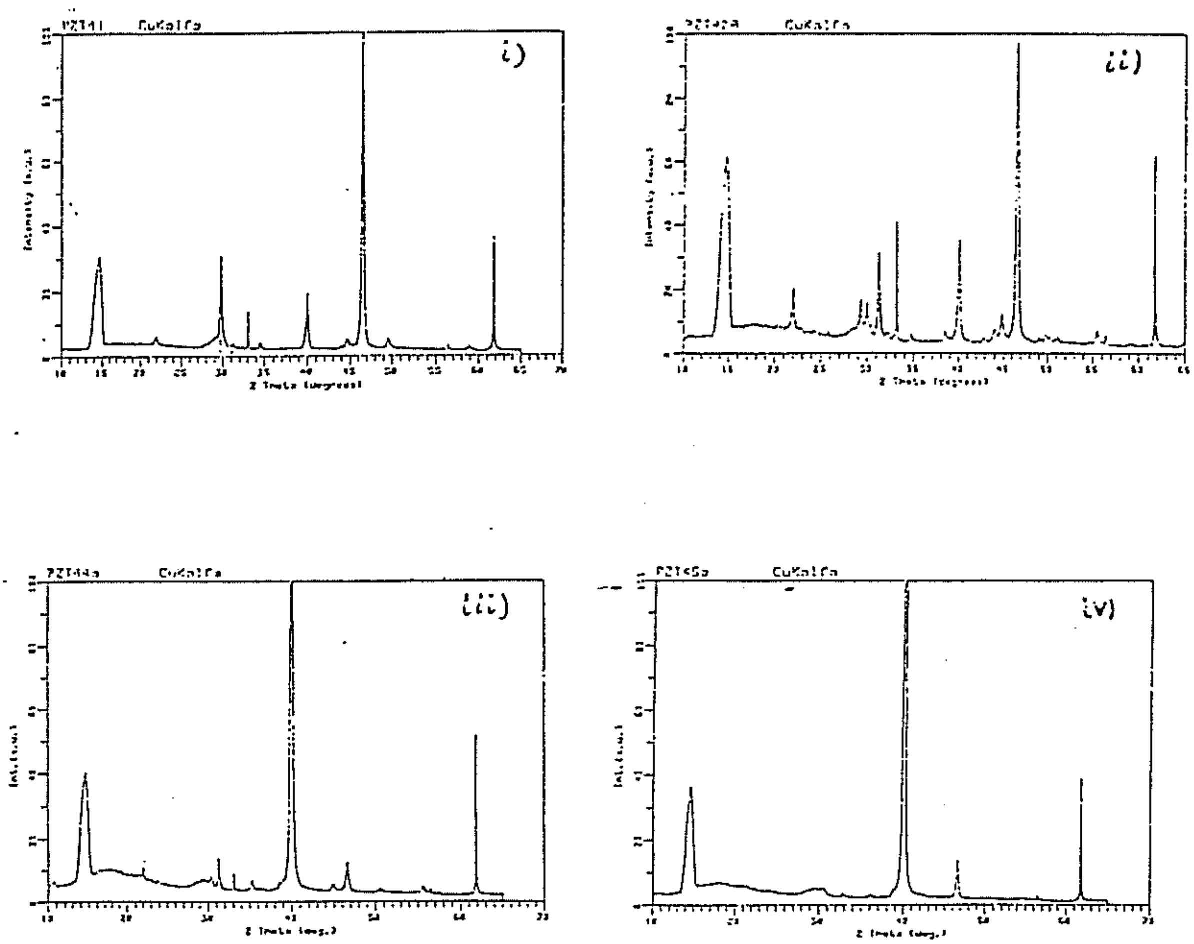

Figure 1. X ray diffraction patterns of PZT deposited on $Si/SiO_2/Ti/Pt$ at i) 453; ii) 490; iii) 527; iv) 564 °C.

The evidence presented in Fig. 1 shows the effect of growth temperature on the formation of the perovskite phase. At the lowest temperature the film is mainly pyrochlore, but at 490 °C and, more so at 527 °C perovskite crystallises. At even higher temperatures both the pyrochlore and perovskite disappear, probably due to excessive lead evaporation, leaving a poorly crystalline film.

Substrate effects.

Different types of substrate were compared and can be divided into two classes: i) single crystal oxides, MgO, $SrTiO_3$; ii) silicon with sputtered conducting electrodes, $Si/SiO_2/Ti/Pt$, Si/RuO_2, $Si/Ti/RuO_2$.

The X ray diffraction patterns of the samples grown on these substrates are shown in Fig. 2.

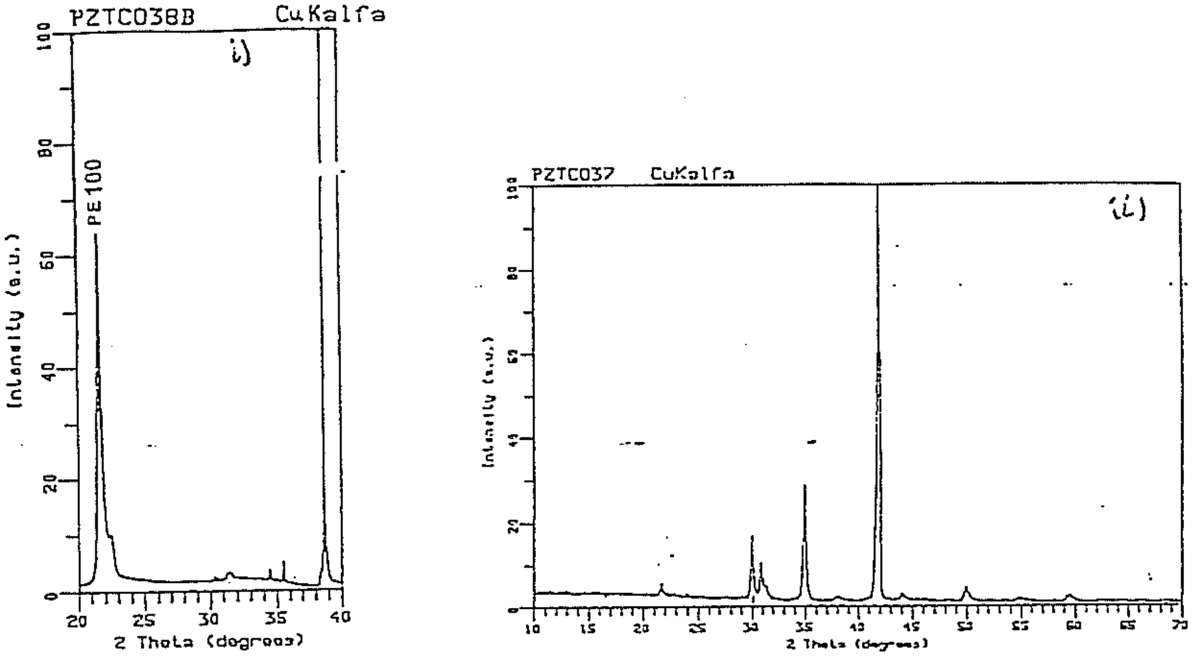

Figure 2. XRD spectra of PZT on i) MgO ii) sapphire.

Target Composition.

Two target compositions were studied, the stoichiometric $PbZr_{0.52}Ti_{0.48}O_3$ and a lead rich composition $Pb_{1.1}Zr_{0.52}Ti_{0.48}O_3$. The results indicate that lead rich targets encourage the crystallisation of the perovskite phase. Lead losses are a particular problem in the growth PZT films due to the volatility of the lead. In fact, excess lead is added to samples prepared by sol-gel both as a fluxing agent to aid crystallisation and to compensate for lead losses, which is most critical in low pressure deposition systems.

Post processing.

The studies on deposition temperature show that at temperatures above 500 °C the ferroelectric phase forms. Another possibility may be to remove residual pyrochlore by annealing after deposition.

Results show that this can be effective. However, films deposited on RuO_2 grew as pyrochlore and annealing in oxygen at temperatures between 650 and 800 °C partially recrystallised the perovskite. phase. An interesting result as obtained when the film was recrystallised at low oxygen pressures. In this case the film was completely perovskite, even though the as grown film was the paraelectric phase.

Discussion and Conclusions

The fact that many different experimental parameters influence the phase formation in PZT films indicates that the deposition of the perovskite by PLD is complex and the preparation of these needs very reproducible procedures. However, several interesting points have been raised in these experiments.

1. It is often assumed that the pyrochlore phase crystallises because of lead deficiency or evaporation; this may be the case at high temperatures, for example when bulk ceramics are sintered it is often done in an overpressure of PbO to avoid the formation of $PbTi_3O_7$. In the case of thin films the pyrochlore phase crystallises at low temperatures which begs the question of why it should form at lower temperatures than the perovskite. In addition, it seems that this phase has the composition $Pb_2Ti_2O_{6+x}$, not lead deficient. Two possible hypothesises may be that either this phase is the more stable at lower temperatures or that its growth is favoured kinetically; careful calorimetric analysis would be required to determine the correct mechanism.

2. Whichever of these two reasons, the assumption that the presence of $Pb_2Ti_2O_{6+x}$ is not due to lead evaporation helps to explain why perovskite should form at higher temperatures, during growth and as a result of post processing.

3. Oxide substrates or substrates which have suitable nucleation sites i.e. RuO_2 and Pt electrodes with Ti help the $PbTiO_3$.

4. The low temperature pyrochlore ($Pb_2Ti_2O_{6+x}$) may contain some Pb^{4+}, this may be reduced either at higher temperatures and at low oxygen partial pressures, helping the transformation to the ferroelectric phase.

References.

[1] H. Rodríguez, B.E. Watts, F. Leccabue, E. Melioli, R. Panizzieri
PULSED LASER ABLATION DEPOSITION FOR PREPARATION OF OXIDE THIN FILMS
MASPEC Internal Report n. 77, September (1994).

European cooperation in the field of scientific and technical research

Annual Report 1994
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Annual Report 1994
COST 514
Ferroelectric Ceramic Thin Films

May 1995

Edited for COST 514 Management Committee by N. Setter and M. Kedro

EUROPEAN CONCERTED ACTION
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KONZERTIERTE EUROPÄISCHE AKTION

COST 514

"FERROELECTRIC CERAMIC THIN FILMS"

"LES FILMS MINCES CERAMIQUES FERROELECTRIQUES"

"FERROELEKTRISCHE KERAMIKDÜNNSCHICHTEN"

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MANAGEMENT COMMITTEE MEMBERS

BELGIUM:	*Dr. D. Wouters Interuniversity Micro-Electronics Center (IMEC) Kapeldreef 75 B - 3001 Leuven*	*Tel: +32-16-281.301 Fax: +32-16-281.501*
	Dr. J. Smeets VITO - Materials Division Boeretang 200 B - 2400 Mol	*Tel: +32-14-333.111 Fax: +32-14-321.186*
DENMARK:	*Dr. Wanda W. Wolny (Ms) Ferroperm A/S Hejreskovvej 6 DK - 3490 Kvistgard*	*Tel: +45-49-13.81.90 Fax: +45-49-13.81.88*
FINLAND:	*Prof. Seppo Leppävuori University of OULU Micorelectronics and Material Physics Laboratories FIN-90570 OULU*	*Tel: +358-81-553.2711 Fax: +358-81-553.2728*
GERMANY:	*Dr. C. Hemminghaus Projektträgerschaft Material -und Rohstofforschung Forschungszentrum Jülich GmbH D - 52425 Jülich*	*Tel: +49-24-61.61.48.89 Fax: +49-24-61.61.23.98*
	Prof. Dr. Ing. Rainer Waser Inst. für Werksstoffe der Elektrotechnik RWTH D - 52056 Aachen	*Tel: +49-241-80.78.13 Fax: +49-241-87.63.89*
ITALY	*Prof. Fabrizio Leccabue Instituto Maspec CNR Via Chiavari, 18 a 43100 Parma*	*Tel: +39-521-269.207 Fax: +39-521-269.206*
IRELAND:	*Dr. John Alderman NMRC University College Cork Ireland*	*Tel: +353-21-27.68.71 Fax: +353-21-27.02.71*

SLOVENIA:
Dr. Marija Kosec (Ms)
Josef Stefan Institute
University of Ljubljana
Jamova 39
SLO - 61111 Ljubljana
Tel: +386-61-125.91.99
Fax: +386-61-219.385

SPAIN:
Dr. P. Duran
Electroceramic Dept.
Instituto de Ceramica y vidrio
Crta de Valencia - K 23.4
E 28500 Arganda del Rey
Tel: +34-1-871.18.00
Fax: +34-1-870.05.50

Prof. Lorena Pardo (Ms)
Dpto. Materiales Ferroelectricos
Inst. Ciencia de Materiales CSIC
Serrano 144
E - 28006 Madrid
Tel: +34-1-561.88.06
Fax: +34-1-411.76.51

SWEDEN:
Prof. K.V. Rao
Dept of Condesed Material Physics
Royal Institut of Technology
S - 110444 Stockholm
Tel: +46-8-790.771
Fax: +46-8-790.7771

SWITZERLAND:
Prof. Nava Setter (Ms)
Lab. de céramique
EPFL MX-D
Ecublens
CH - 1015 Lausanne
Tel: +41-21-693.29.75
Fax: +41-21-693.29.35

TURKEY:
Prof. Macit Ozenbas
SEKOM
Dept. Metallurgical Engn.
Middle East Technical University
06531 Ankara, Turkey
Tel: +90-312-210.10.00
Fax: +90-312.210.12.67

UNITED KINGDOM:
Mr. B. Kerrison
Department of Trade & Industry
IMT Dvision
151 Buckingham Palace Road
UK - London SW1W 9SS
Tel: +44-71-215.15.19
Fax: +44-71-215.29.09

EUROPEAN COMMISSION:
Dr. Martin Kedro
Rue de la Loi,200
MO 34 0/10
B - 1049 Bruxelles
Tel: +32-2-296.55.12
Fax: +32-2-296.59.25

Editorial note

The Appendices 2 and 3 represent more than 200 pages each and are printed separately as Supplement I and Supplement II.
The reproduction was done using copies of transparencies which were often of very low quality.

mk

COST 514 "FERROELECTRIC THIN FILMS"

INTRODUCTION

The objective of this COST Action is to initiate and promote a coordinated European effort for the development of ferroelectric thin films with and for European industries. In particular it is meant to encourage fundamental research targeted at technological problems that have been slowing down the introduction of ferroelectric thin films into commercial products.

17 project proposals have been submitted before the deadline of 15.10.1993. The Management Committee evaluated them at its meeting on 18.11.1993 and accepted 16 projects. These 16 projects, later during 1994 extended to 18 accepted projects, are structured in 4 group projects. Since the projects are complementary, the reports are in general distributed and discussed with all the participants of the COST 514 Action.

The research has started during 1994 in all the groups, in spite of uncertainty with regards to financing of the work in most of the cases. Group project leaders have been assigned, and the coordination and interaction between the groups have been established. The running of the program has been discussed, reviewed and controlled during the Management Committee meetings of 7.5.1994 (Stockholm) and of 4.9.1994 (Aachen).

A start-up workshop has been organised by Prof. Rao of the Swedish Royal Institute in Stockholm on 6.-7.5.1994. The invited speakers were from industries such as Philips, Siemens, GEC-Marconi, Belcore, Rockwell International, Matzushita, Sanyo and from universities. Participants came from many European industries and academic laboratories. The workshop has ended with a panel discussion concerning the future of ferroelectric thin films. The workshop has been very useful due to the large scope of active participants. The abstracts of the lectures and posters presented at the workshop are enclosed (Appendix 2).

The work accomplished during 1994 has been presented in a workshop that has been held in EPFL in Lausanne on 16.-17.2.1995. 18 presentations have been given, covering all the projects in the program. Invited plenary lectures were given by Prof. D. Smyth from Lehigh University (USA) and Dr. W. Wersing from Siemens. The program of the meeting and copies of the transparencies are enclosed (Appendix 3). The copies of transparencies show the advances made during the first year of the action.

Reports on the research carried out in the projects are enclosed below (Appendix 1) together with the summaries of the group-project leaders. The 4 group projects deal all of them with thin film processing and their characterisation. Depending on the group-project the work is oriented toward microelectronics ("Materials for a ferroelectric capacitor stack with direct contact to silicon") toward communications ("Ferroelectric ceramic thin films for SAW devices"), and toward sensors, actuators and capacitors ("Reliability of ferroelectric thin films"). One project is centred at laser ablation processes ("Pulsed laser ablation deposition of ferroelectric thin films") but many groups use the chemical route (sol-gel route) for the processing of the films. Variety of ferroelectric films are studied: lead zirconate-titanate, modified lead titanate, strontium titanate, lead scandium tantalate, also variety of electrodes (metals and oxides) are being studied by the different groups. Structural characterisation is done by electron microscopy and by X-ray diffraction methods - by groups who have long-standing reputation in these methods. Functional characterisation: electrical, dielectric, piezoelectric, optical methods are used, in many cases specifically developed during the present action. Devices have been designed and first tests have been performed although naturally, the first period of the program is an early stage for device fabrication.

It is too early to make a synthesis of the results, but one important trend should be underlined. In fact the 18 laboratories participating in this program have close relations and the information exchange between all the groups is very open. Because of the complementarity of the laboratories, the action covers a wide area and it is expected that the work done within this program will be very valuable in future ferroelectric devices.

Appendix
Group project reports

Report Title	Partner: • Laboratory • Country • Collaborators	

RELIABILITY OF FERROELECTRIC THIN FILMS

SUMMARY REPORT: M. Kosec		
• Study of the Crystallization of PZT Thin Films by High Temperature XRD	• Lulea University of Technology • SWEDEN • O.Babushkin	
• IJS activities report in year 1	• "Josef Stefan" Institute, University of Ljubljana • SLOVENIA	
• Analytical Electron Microscopy Study of Sol-Gel Derived PLZT Thin Films and Powders	• "Josef Stefan" Institute, University of Ljubljana • SLOVENIA • G.Drazic et al.	
• TEM of Ferroelectric Thin Films	• University of Sheffield • UK • I.Reaney	
• Reliability of Ferroelectric Thin Films	• LC/EPFL • SWITZERLAND • A.Kholkine	
• Recent Results on Relaxation, Conduction and Breakdown of Perovskite-Type Dielectric Thin Films	• RWTH Aachen • GERMANY • G.W.Dietz et al.	

PULSED LASER ABLATION DEPOSITION OF FERROELECTRIC THIN FILMS

SUMMARY REPORT: K.V. Rao		
• Pulsed Laser Deposition of Ferroelectric Thin Films	• University of Oulu • FINLAND • S.Leppävuori et al.	
• Pulsed Laser Deposition of Ferroelectric Thin Films	• Salford University • UK • A.E.Hill et al.	
• Investigation of PLD PZT Thin Films	• University College London • UK	
• Pulsed Laser Ablation Deposition of Ferroelectric Thin Films	• Royal Institue of Technology • SWEDEN • K.V.Rao et al.	

FERROELECTRIC CERAMIC THIN FILMS FOR SAW DEVICES

SUMMARY REPORT:	• ICMM SPAIN • Ferroeperm • DENMARK • Univ. of Manchester • UK	
• Advances of Preparation and Characterization of Ca Modified Lead Titanate Thin Films	• J. Mendiola • CSIC • SPAIN	

MATERIALS FOR A FERROELECTRIC CAPACITOR STACK WITH DIRECT CONTACT TO SILICON

SUMMARY REPORT:		
Materials for...	• IMEC • BELGIUM • D.Wouters et al.	
• Laser Deposition of PZT Thin Films and In-Situ Diagnostics of the Process	• Univ. of Pisa • ITALY • F.Fuso et al.	
Materials for...	• VITO • Univ. of Pisa • ITALY	
Materials for...	• MASPEC • Parma, ITALY • B.Watts	
• Novel Polarized Ferroelectric Thin Films for Silicon Integrated Devices	• IPA-EPFL • SWITZERLAND • P.H.Schmid et al.	

APPENDIX: NOVEL PROCESSING METHODS

• Preparation and Characterization of Ferroelectric Thin Films by Sol-Gel Processing Using Urea	• Middle East Technical University • TURKEY • M.Ozenbas	

Summary of the activities in the year 1994
COST 514 - Ferroelectric Thin Films

Group project: Reliability of Ferroelectric Thin Films

Participants:	B1:	IMEC. Division MAT - ARS. Leuven. Belgium. Dr. D. Wouterss (IMEC)
	CH1:	EPFL. Laboratoire de Céramique. Lausanne. Switzerland. Prof. N. Setter (EPFL)
	D1:	RWTH Aachen. Institut für Werkstoffe der Elektrotechnik. Aachen. Germany Dipl. Ing. G. Dietz (RWTH)
	SLO1:	"Jožef Stefan" Institute. Ljubljana. Slovenia. Dr. M. Kosec (IJS)
	S2:	Luleå University of Technology. Div. of Engineering Materials. Luleå. Sweden. Dr. T. Lindbäck and Dr. O. Babushkin (LuTH)
	UK4:	University of Sheffield. Dept. of Engineering Materials. Sheffield. England. Dr. W. Lee and Dr. I. M. Reaney (Sheffield)

The group project includes research topics related to the realibility of ferroelectric thin films. namely processing. structural and functional characterisation.

Several significant results have been obtained. Not all but some of them are briefly summarised as follows. For details see the individual group reports.

Processing of electrode and FE films (IMEC, IJS)

IMEC and IJS are strongly involved in this topic. IMEC compared the crystallization behaviour and hysteresis properties of laser ablated and sol-gel derived PLZT films on identical substrates.

They came to the important consclusions, namely the properties of the films are mainly limited by the quality of electrode and not by the deposition method used. With another words sol-gel methods might result in high performance PZT films. IJS studied the sol-gel processing of PZT and PLZT thin films. They showed how the crystal structure and microstructure were controlled by the precursors used. They also demonstrated that the preferentially oriented, relatively thick (0.5 μm) films of PZT could be processed in a single step using diol routes.

Structural characterisation related to processing and functional properties, respectively (LuTH, IJS, Sheffield)

LuTH has just identified a number of problems related to in-situ high temperature X-ray study of crystallisation process of PZT amorphous layers. The measurements were realised on samples supplied by EPFL. IJS used analytical electron microscopy to study not only the structure but also the composition of the coexisting phases in PLZT layers after heat treatment at different temperatures. A tentative mechanism of pyrochlore to perovskite transformation was proposed. Sheffield demonstrated the significance of chemical composition i.e. Zr/Ti ratio in the domain structure of PZT films.

Functional characterisation (EPFL, IMEC, RWTH)

Pioneer work was done on piezoelectric characterisation of PZT films at EPFL. They started by setting up the equipment and continued by the systematic measurements of piezo response of films under different conditions. including the conditions imitating the work of piezoelectric ultrasonic motor.

Finally IMEC and RWTH investigated the relaxation, conduction and brake-down behaviour of non-ferroelectric and ferroelectric thin films. The results obtained concern the detail analysis of measurement techniques, measurement and careful modelling of selected phenomena.

Concerning the organisation it has to be noted that two additional groups joined the Reliability of Ferroelectric Thin Film project in 1994. LuTH is highly qualified in high temperature XRD and the Sheffield group in structural characterisation by TEM. STEM and HREM. Therefore their contribution is mainly on structural characterisation of thin films related to their properties and functional characteristics.
There were group meetings on 04. 09. 1994 in Aachen and on 17. 02. 1995 in Lausanne that resulted in exchange of results and plans for further cooperation. From the same reasons there were also bilateral visits as from EPFL to RWTH and from IJS to EPFL and RWTH.

The samples from EPFL were used in investigations at LuTH. EPFL samples were used at IJS to check the dielectric measurements. Pt coated Si-substrates from EPFL were sent to IJS. In future, all groups continue the research. Further cooperation include the exchange of results as well as the exchange of samples. Therefore substrates from EPFL and IMEC will be sent to IJS where the FE layers will be processed and sent back for measurements. This will help to clarify the role of the substrate in functional properties of films. In-situ crystallisation studies will be done on samples from different labs (EPFL, IJS).

Ferroelectric Thin Films

Subprogram: Characterization

Luleå University of Technology
Division of Engineering Materials

European Concerted Action
COST 514

Activity

1 Nov 1994 to 31 Jan 1995
(our activities have only been running for three
months because of a delay in the financing)

Purpose of the project

The aim of this project is to study the crystallisation of ferroelectric amorphous thin films based on PZT compositions, with application of high temperature X-ray technique.

Experimental procedure

The nucleation and growth kinetics of the perovskite phase was studied on thin films prepared on Si substrates with a buffer layer of SiO_2 and Ti/Pt electrode metallizations.

The films were supplied by Dr. K. Brooks at EPF in Lausanne and may be classified into two main groups with respect to the state of the Pt substrate;

A) films based on highly oriented (111) Pt (Fig. 1).

B) films based on randomly oriented Pt (Fig. 1).

In situ X-ray diffraction investigations were performed with a Philips PW-1710 automatic diffractometer equipped with a high-temperature attachment engineered by the authors. Continuous scanning was performed with Cu Ka radiation (50 kV, 30 mA) and a graphite momochromator. Diffractograms were collected from 20,0–50,0 2θ for all samples. In order to control the profile development of the PZT (110), (100) and pyrochlore peaks growing on the randomly oriented Pt film, two subscans within 21,6–22,8 2θ and 27,5–32,0 2θ were performed. The temperature of the sample was measured with a Pt-13/Rh/Pt termocouple. In-situ investigations of the phase development were performed during isothermal heat treatment in the temperature range 500–700 °C with a maximum soaking time of 60 minutes.

Quantitative phase analysis requires accurate measurements of the integrated intensities of the diffracted lines. Obviously, when the lines are isolated and on simple backgrounds, count intergration techniques work wery well. However,

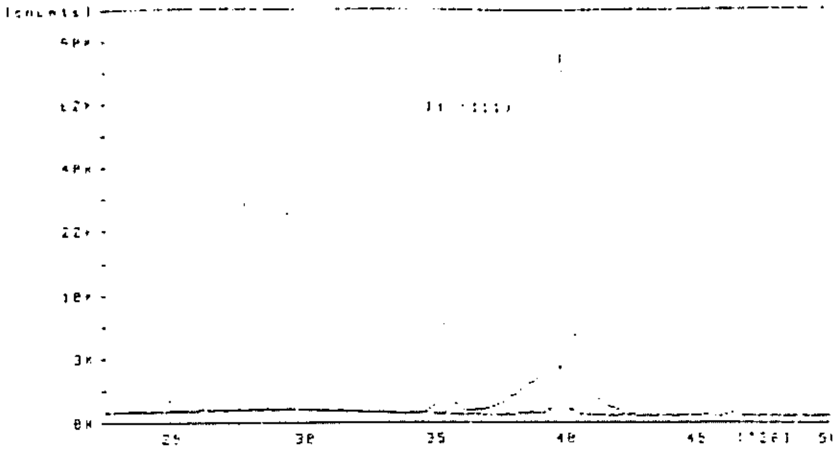


Fig1. Fragments of films deposited on randomly and high oriented (111) Pt substrate.

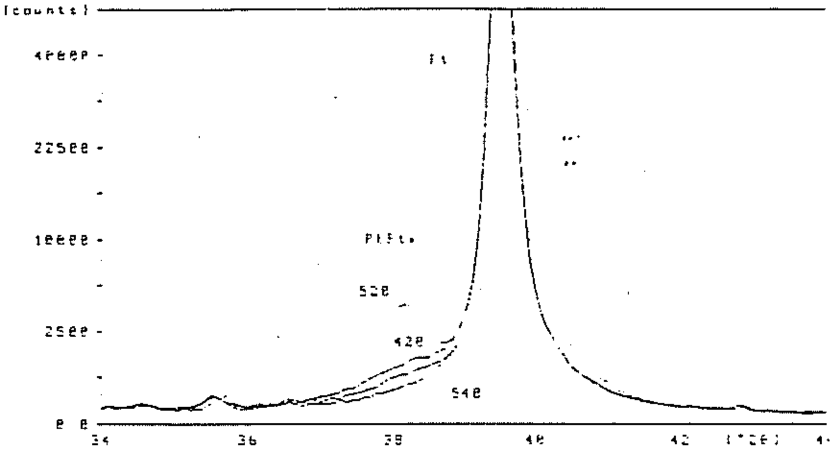


Fig2. Illustration of the development PbPt$_x$ phase.

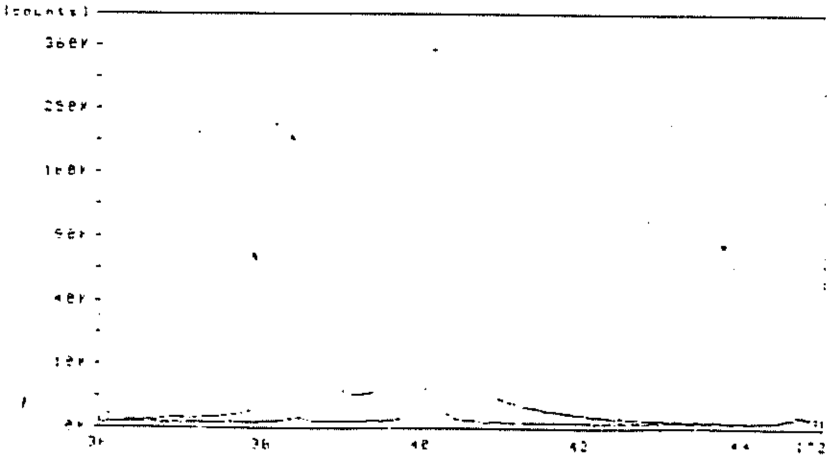


Fig3. High textured (111) PZT film after crystallisation at 650°C

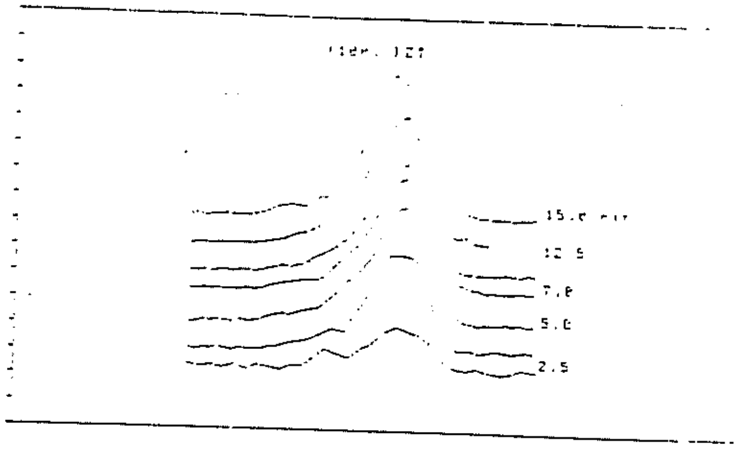


Fig.4 Profile shape of the PZT (100) peak for different time at 670°C

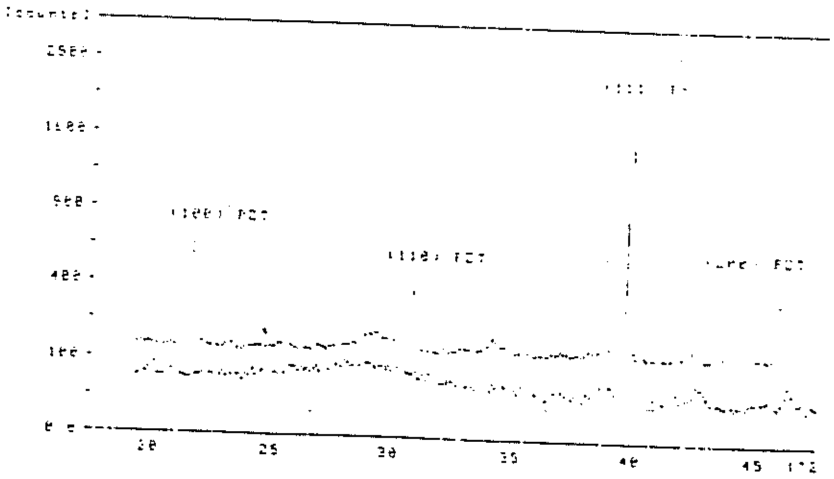
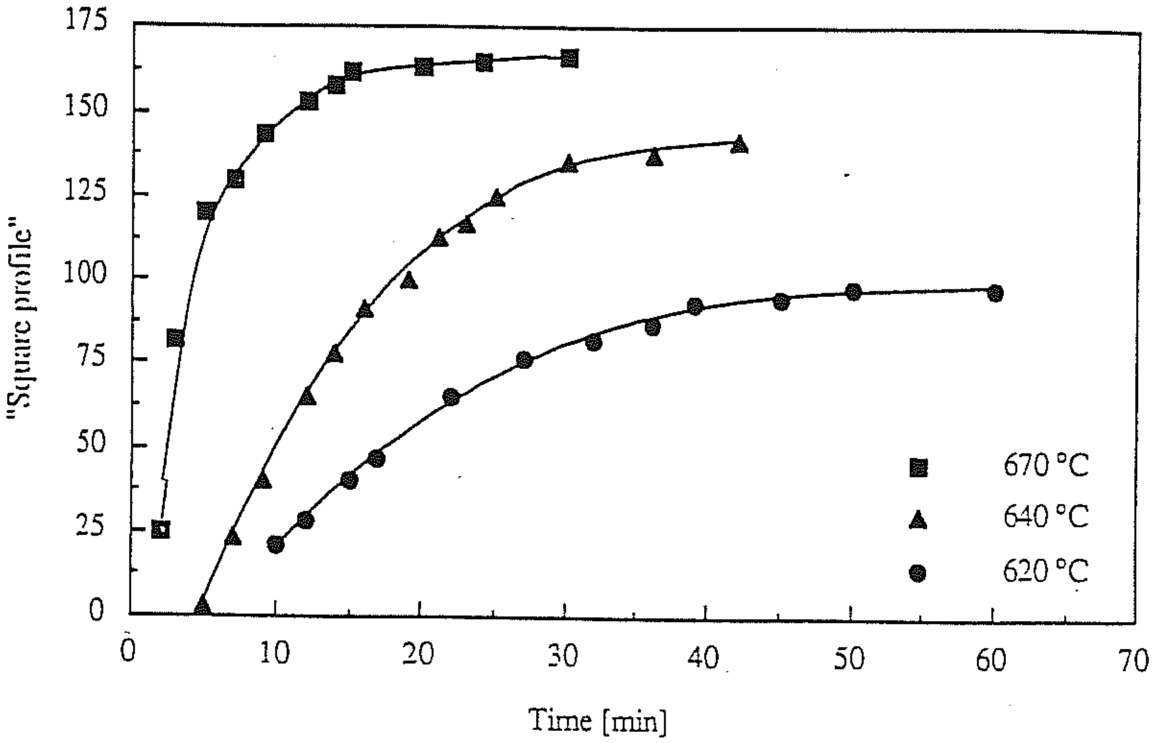
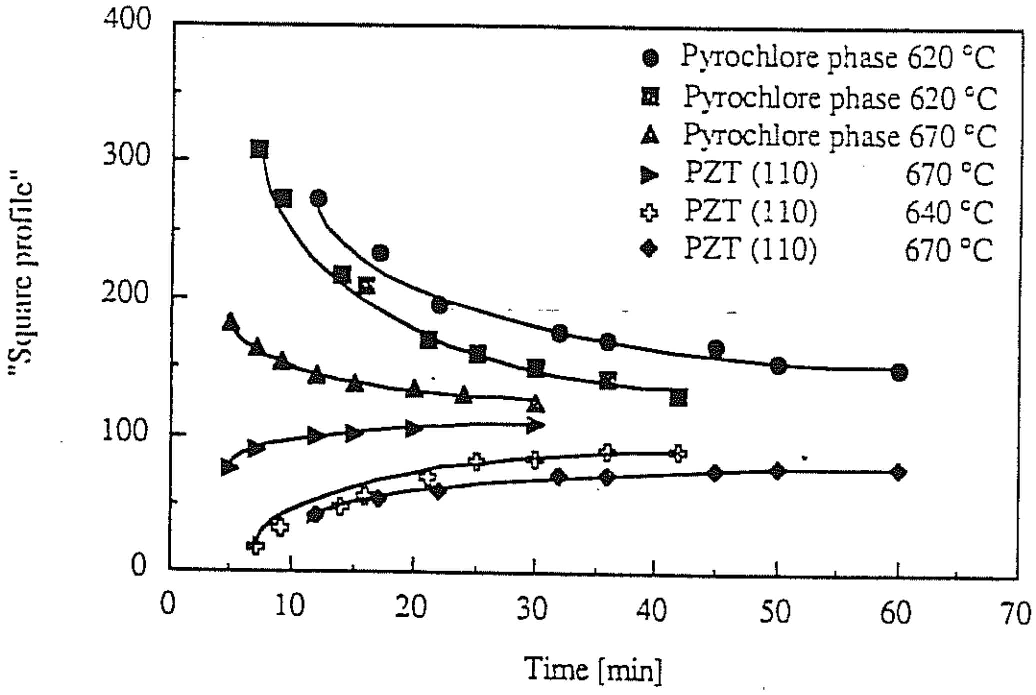


Fig5. Diffraction patterns of the PZT thin film before and after heat-treatment at 670°C.



Integrated intensity of the (100) peak of the PZT phase at different temperatures versus time.



Integrated peak intensities of the pyrochlore and PZT (110) phases versus time.

when one or several lines overlap the line of interest, or when a complex background is present, profile fitting techniques are required in order to eliminate interferences. To solve these problems, a profile model based on assymetric Lorentzians for fitting the instrument and wavelength related components of a powder diffraction profile together with a Marguardt non-linear least squares algorithm were used for fitting the main (100), (110) and (111) peaks of the PZT phase.

To summarise, the following results have been obtained:

A. Film deposited on a highly oriented substrate.

1. During dynamic heat treatment, the formation of a metastable $PbPt_x$ phase was detected. The stability range was within 420–540 °C (fig. 2.)

2. The strongly textured (111) PZT film was crystallised in the temperature range 600–700 °C (Fig. 3.). Because of a very high transformation rate of the crystallisation of the amorphous film, additional experiments are required in order to clarify the rate of this process.

B. Film deposited on a randomly oriented substrate.

1. After crystallisation the film is characterised by a slight formation of a PZT phase with a preferable (110) oriented crystal growth (Fig. 4, 5.).

2. The crystallisation process in the temperature interval 620–670 °C, can be refered to the known transformation of metastable pyrochlore phase to stable PZT phase.

3. In situ observations have been performed on the development of the two (100) and (110) main peaks of the PZT phase. The integrated intensities of these profiles as well as that of the pyrochlore phase (Fig. 6.) will be used as a basis for further kinetic analysis of the crystallisation process.

COST 514: Reliability of Ferroelectric Thin Films

IJS activities report in Year 1

M. Kosec

In accordance with IJS proposal the work has been focused on sol-gel processing of PZT based thin films and their structural characterisation.

In experiments films were posited on Pt coated Si-substrates obtained from EPFL.

i) Sol-gel processing of PZT

Two solvent systems were used for the processing of PZT thin films. Methoxyethanol route results in ~ 0.5 μm thick film after deposition of 5 layers, whereas ~ 0.5 μm thick films are obtained in a single processing step using diol route. Both films are preferentially 110 oriented.

The microstructure of films is significantly improved by the use of PbO instead of $Pb(OAc)_2$ (Fig. 1, Fig. 2).

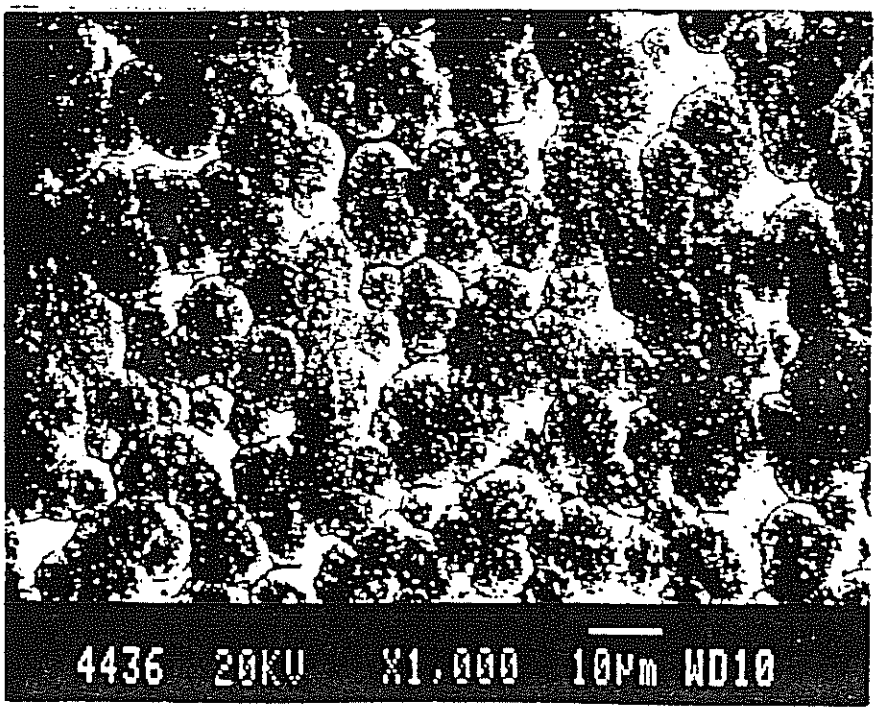


Fig. 1: SEM micrograph of PZT film prepared from $Pb(OAc)_2$, annealed at 700°C, 10 min.

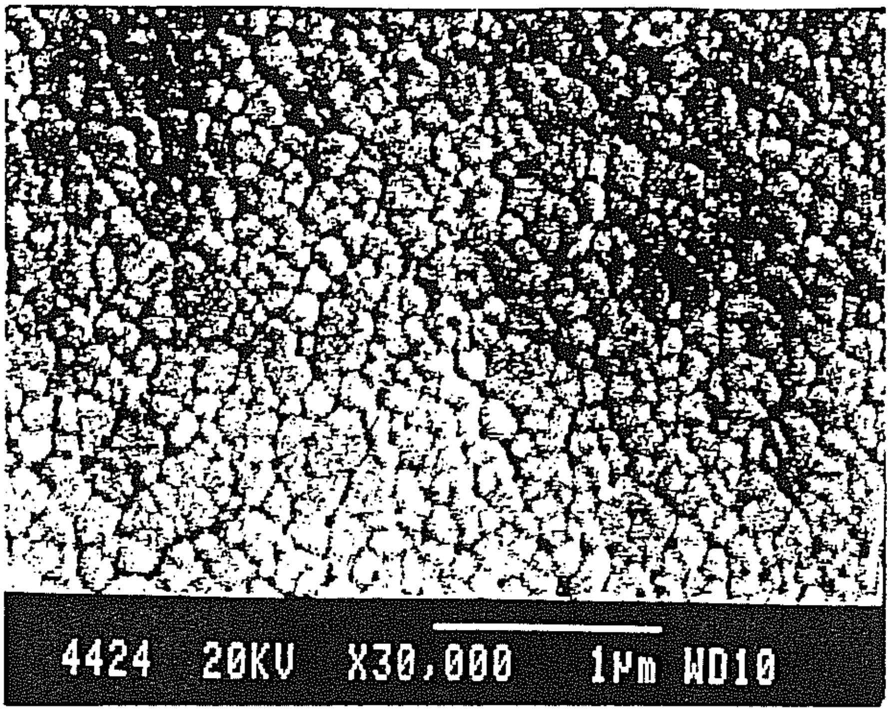


Fig. 2: SEM micrograph of PZT film prepared from PbO, annealed at 700°C, 30 min.

ii) Several processing parameters have been varied in order to get well crystallised, low pyrochlore content, microstructurally homogeneous PLZT thin films of compositions 8/65/35, 9.5/65/35, and 2/95/5. These parameters are the amount of PbO excess, precursor chemical composition, and solvent. The amount of PbO influences the orientation of films. Films processed by diol route require higher annealing temperatures. There are still not enough reliable results to make further conclusions.

iii) The crystallisation of PLZT 9.5/65/35 powder and films deposited on Pt coated Si.
Sol-gel PLZT powders and PLZT thin films on Si/Ti/Pt substrates were prepared from a sol with the composition 9.5/65/35, with 10 mole % of excess PbO added. Samples were fired at temperatures between 500°C and 800°C for 10 min. Using an analytical electron microscopy (AEM) the chemical composition, degree of crystallisation, and particle size of phases present were investigated. In both types of samples (powder and thin films) it was found that the size of pyrochlore grains increased with increasing temperature, the chemical composition of

pyrochlore phase became enriched in Zr and La, and the Zr/Ti ratio in perovskite phase decreased with increasing firing temperature. At intermediate temperatures (500°C - 600°C) Pb and PbO crystalline particles were observed in powder samples. Considering the result of quantitative EDXS analysis a tentative explanation of pyrochlore to perovskite phase transformation is described in the paper presented at the workshop "Ferroelectric Thin Films" (this book).

ANALYTICAL ELECTRON MICROSCOPY STUDY OF SOL-GEL DERIVED PLZT THIN FILMS AND POWDERS

Goran DRAŽIČ, Marija KOSEC, Barbara MALIČ and Uroš DELALUT
"Jožef Stefan" Institute, University of Ljubljana
Jamova 39, SI-61111 Ljubljana
Slovenia

A microstructure of a sol - gel derived PLZT thin films on substrates usually consists of monocrystalline and preferentially oriented rosettes of perovskite phase, surrounded by a certain amount of fine-grained Zr-rich pyrochlore phase. Sol composition, type of substrate and electrode used, film thickness and firing conditions influence strongly the volume ratio of perovskite and pyrochlore phases.

In our previous work, where different substrates were used (SiO_2, MgO, Si/Pt substrates with substantial amount of pores in Pt layer) we found that the chemical composition of the perovskite and pyrochlore phases is affected by the firing temperature and the composition of the substrate used. These phenomena were explained by the loss of PbO due to evaporation (to a minor extent) and to the reaction of PLZT material with the Si/Pt-based substrates. An amorphous Pb-Si-O layer was found at the PLZT/Pt/Si interface.

In the present work PLZT powders and thin films on Si/Ti/Pt substrates were prepared from a sol with the composition 9.5/65/35, with 10 mol.% of excess PbO. Using analytical electron microscopy (AEM), the chemical composition, degree of crystallization and particle size of the phases present in the samples were investigated.

A PLZT sol with composition $Pb_{1-3x/2}La_x(Zr_{0.65}Ti_{0.35})O_3$ was prepared from a solution of Ti and Zr n-propoxides, La iso-propoxide and PbO in 2-methoxyethanol under a dry Ar atmosphere. 10 mol.% excess of lead oxide was added to the composition. A clear sol was obtained by heating and refluxing the mixture of precursors in the solvent for 12 hours, followed by distillation. The concentration of the sol after distillation was 0.5M. 4 vol.% formamide was added to the sol after cooling to room temperature. After gelation, the gels were dried at 150 °C and fired at various temperatures in the range between 500 °C and 800 °C for 10 min. Thin films, 400 nm thick, consisting of five layers, were deposited on Pt/Ti/Si substrates by spin coating techniques. Films were pyrolyzed at 350 °C for 1 min. (each layer) and fired at 600 °C, 700 °C and 800 °C for 10 min. in air. Heating rates were around 10 °C/s in all cases.

Powder samples were ground in ethanol and ultrasonically dispersed on a hollow carbon coated Cu grid for AEM investigations. Plan-view specimens of thin film samples for AEM study were prepared by mechanical thinning, dimpling and ion milling with 3.8 keV argon ions from the substrate side. Samples were examined by transmission electron microscopy (TEM), using a Jeol 2000 FX, operated at 200 kV. The chemical composition of phases was determined using a Link AN-10000 EDXS system (Energy Dispersive X-ray Spectroscopy) with an Ultra Thin Window Si(Li) detector, connected to the TEM. The Cliff-Lorimer method and absorption corrections were used for quantitative analysis. The accuracy of the concentration measurements for the elements Pb, La, Zr, Ti were better or equal to 5 %. The concentration of oxygen was calculated from stoichiometry.

After firing thin films at 600 °C, spherical perovskite (P) rosettes (two dimensional spherulites), with a diameter around 1.5μm, surrounded by substantial amount of fine-grained pyrochlore (Py) phase were observed. The rosettes were mostly isolated, with smooth edges and without visible defects. Between the rosettes few perovskite nuclei with the similar orientations as the rosettes were found.

Volume fraction of pyrochlore phase is reduced drastically as the firing temperature increased. Already at 700 °C some areas of the thin film were uniformly covered with intergrowing rosettes, with high number of pores at the rosette-boundaries, where traces of Py phase were also detected. Using selected area electron diffraction and microdiffraction techniques, it was found that rosettes are mainly oriented in <100> or <110> directions (assuming a pseudo-cubic structure) perpendicular to the substrate. Boundaries between rosettes (grain boundaries) are of large-angle type, indicating that there is no preferential orientation of the rosettes in directions parallel to the substrate.

From dark field images the particle sizes in the Py phase, which was detected in all thin film samples, were estimated. It was found that the size increased with increasing temperature as shown in Tab. 1.

Firing temperature	Powder samples	Thin films
500 °C	≤ 2 nm	
600 °C	5 nm	5 nm
700 °C	8 nm	7 nm
800 °C	13 nm	10 nm

Table 1. Particle size of the pyrochlore phase in powder and thin film samples vs firing temperature.

Using quantitative EDXS analysis the chemical composition of perovskite and pyrochlore phases in PLZT thin films were studied. In the perovskite phase a slight decrease of La and Zr concentration and an increase of the ZrTi/PbLa ratio (ratio of elements at sites B to elements at sites A in perovskite structure) were observed in samples fired at higher temperature. The pyrochlore phase was enriched in La and Zr content and depleted in Pb content at higher temperatures compared to the starting composition.

In powder samples fragments of phases with adequate thickness were chosen for the AEM study. In a sample fired at 500 °C several microcrystals of Pb were found beside an amorphous phase and small areas of Py phase. At 600 °C and 700 °C, beside pyrochlore and perovskite phases PbO crystals were also observed in powder samples. However, in samples fired at 800 °C, only perovskite phase and traces of pyrochlore phase were found.

In powder samples we also observed the influence of firing temperature on the particle size of the Py phase (Table 1.). The influence of the firing temperature on chemical composition of the perovskite and pyrochlore phases in powder samples was similar to the influence, found for thin film samples. Pyrochlore phase was depleted in Pb but enriched in

La and Zr content at higher firing temperature while perovskite phase was slightly depleted in the content of La and Zr.

From these results we can conclude that a phase separation took place in powder samples at temperatures around 500 °C. In this temperature range the local partial pressure of oxygen around powder particles is most probably relatively low due to the combustion of organic radicals. Presumably, atoms of lead are not homogeneously distributed in the gel structure but are concentrated in micro regions. During the firing process lead is separated, reduced to elemental Pb and melted. On cooling it forms around 20 nm large crystals. At higher temperatures, where most organics are already burnt out, lead is oxidized to PbO, which could react with surrounding matrix or evaporate. The appearance of Pb and PbO microcrystals was also observed in powder samples with similar composition, but without an excess of PbO. In thin film samples we did not detect Pb or PbO phase.

An increase of the pyrochlore particle size and a simultaneous enrichment of this phase in La and Zr content and reduction of Pb content with increasing firing temperature was observed in powder and thin film samples.

A tentative explanation of the Py particles formation could be as follows:
At around 500 °C a few nm large Py particles are nucleated inside an amorphous matrix which has a composition close to the starting one. The chemical composition of the Py particles alone could not be determined by AEM due to their small size, so only the average concentration of Py particles and amorphous phase could be measured. At higher temperatures (600 °C and over) the PbO from the amorphous matrix evaporates (the vapour pressure of PbO in the amorphous phase is expected to be much higher than the vapour pressure of PbO in the pyrochlore or perovskite phase), so that the amorphous phase become more and more Pb deficient. Simultaneously with these processes, the crystallization of perovskite phase is taking place from the amorphous phase. Extreme reduction of the volume percentage of pyrochlore phase (Py particles in an amorphous matrix) relative to the perovskite phase at higher firing temperatures indicates that Py phase transforms to P phase. This transformation is presumably accomplished through the amorphous phase, i.e. Py particles are in dynamic equilibrium with the amorphous phase, so that they crystallize and could be again dissolved after some period of time.

In this explanation Py particles are postulated as nuclei with subcritical size, so that they could not grow. Finally, the amorphous phase disappears and only Py particles with a high Zr and La and low Pb content and perovskite grains with slightly Zr and La deficient composition remain in the samples. Due to the lack of PbO the pyrochlore phase could not be completely transformed to the perovskite one.

It was found that the d values of the pyrochlore phase (cubic structure with a_0 = 1.04 nm), measured from the electron diffraction patterns, are practically the same (within the range of experimental error) in all samples, regardless the chemical composition.

TEM of Ferroelectric Thin Films

by

Ian M. Reaney

Department of Engineering Materials,
University of Sheffield, Sir Robert Hadfield Building,
Mappin St., Sheffield, S1 4DU.

Summary

Transmission electron microscopy (TEM) has been used to investigate the interfaces and the domain structures associated with Pt/PZT/Pt/Ti(TiO_2)/SiO_2/Si ferroelectric stacks. The domain structures associated with *in situ* sputtered films and fine grained solution-gel material were complicated with an average domain width of about 20nm. Larger grained solution-gel material had a more ordered domain structure with boundaries lying on {110} planes.

The interface between the bottom electrode of the film was of a general high quality provided that the deposition process was optimised. However, solution gel thin films exhibited pyrochlore inclusions between the top electrode and the film which were present because of poor PZT crystallisation. In situ reactive sputtered films showed a superior interface.

Results and Discussion

The ferroelectric and piezoelectric properties of bulk ceramics are often related to the behaviour of domains under applied field or stress. The domain structures in bulk ferroelectric materials have been well investigated and the contribution associated with domain wall motion is understood. Domain structures and textures in ferroelectric thin films remain relatively unknown. Consequently their influence on electrical properies is an open question. Here, some preliminary results are shown which illustrate the domain structures for FE thin films deposited by solution-gel spinning and reactive sputtering.

Figures 1 is a TEM image which shows the domain structure associated with an in-situ reactive sputtered film. The mottled fringe contrast is indicative of a complicated domain structure with an average domain width of about 20nm. Although, domain structures can be alterred during TEM preparation because of the release of clamping restrictions in the z-dimension, it is unlikely that this would result in such a complex arrangement. In general, stress relief of this nature would be expected to give rise to a more simple distribution of domain walls. Furthermore, the domain width (20nm) is considerably smaller than the sample thickness (200nm) and clamping of these regions will still exist. It is suggested that these observations are more likely to be related to the presence of extended and point defects in the PZT thin film which interact with the domain walls and limit the domain width. Fine grained solution gel PZT exhibits a similar domain structure. A more conventional domain structure is observed in larger grained films with domain walls lying on {110} planes. More study is necessary if these results are to be understood and related to properties.

Several recent publications have suggested that the quality of the

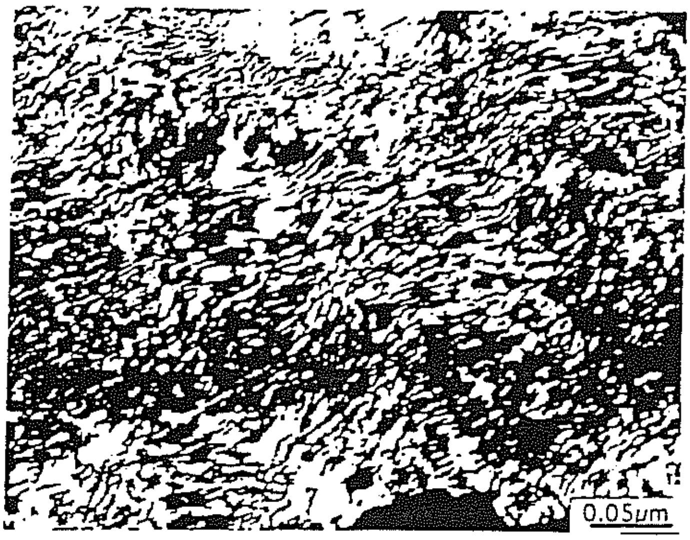


Figure. 1 Dark field TEM image obtained using a {110} reflection which shows the complex domain structure frequently observed in PZT thin films.

film/electrode interfaces is an important parameter in the switching characteristics of FE thin films. When conditions of deposition are optimised, the bottom electrode/film inteface is of generally good quality for all deposition techniques. For films grown by in-situ deposition methods (MOCVD and in-situ reactive sputtering), the top electrode/film interface can also be of high quality with an almost atomic scale bond. However, films grown by ex-situ techniques such as solution-gel spinning contain inclusions of pyrochlore between the electrode and film, figure 2. These arise from poor crystallization of PZT at the film surface, resulting in the retention of a Pb-deficient, Zr-rich, pyrochlore phase.

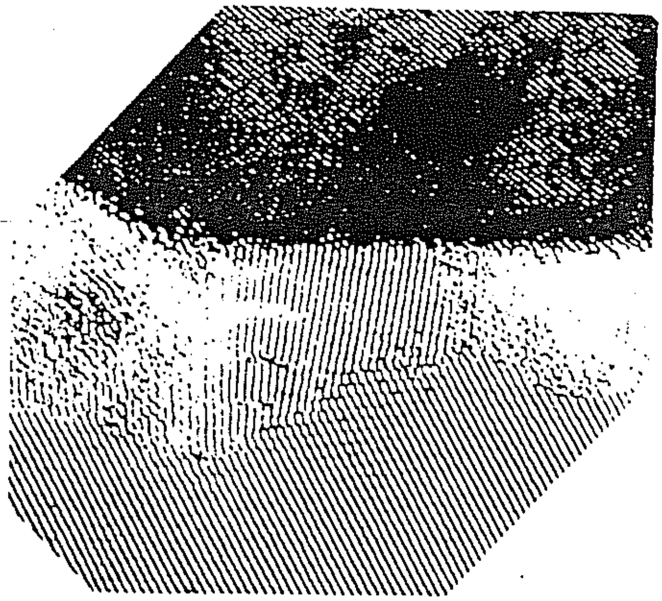


Figure 2. High resolution transmission electron micrograph of the top/electrode film interface in a solution-gel deposited thin film.

RECENT RESULTS ON RELAXATION, CONDUCTION, AND BREAKDOWN OF PEROVSKITE-TYPE DIELECTRIC THIN FILMS

Guido W. Dietz and Rainer Waser
Institut für Werkstoffe der Elektrotechnik (IWE)
RWTH Aachen University of Technology
52056 Aachen, Federal Republic of Germany

1. Introduction

In this paper, we report briefly about some of our recent results on relaxation, conduction, and breakdown of perovskite-type dielectric thin films. After discussing the advantages and disadvantages of the voltage-step technique on the one hand and the voltage-ramp technique on the other hand, we introduce an electrical equivalent circuit, based on experimental data, for non-ferroelectric titanate thin films. Current responses to voltage-steps and voltage-ramps are calculated. Experimental evidence is given that the leakage current in $SrTiO_3$ thin films is controlled by thermionic emission. Some new results on breakdown of $SrTiO_3$ thin films are presented.

2. Experimental

The importance of the voltage-step technique for the analysis of dielectric thin films was already pointed out in 1992 [1]. The principle of the voltage stimulation and the current response are described in some detail in [2]. The main advantages of the voltage-step technique are:

- Clear distinction between relaxation currents and leakage currents if charging and discharging currents are compared.
- The high-frequency capacitance is charged immediately when the voltage-step is applied and, therefore, does not influence the measurement thereafter [3].

The voltage-ramp technique is very well known from the characterization of semiconductors where I-V-recorders are employed frequently. A voltage-ramp with constant slope is applied to the sample and the resulting current is measured. In thin film characterization this method is well established, too. An advantage of the voltage-ramp technique is that I-V curves are directly generated in only one measurement. Voltage-ramp experiments in general contain information about the high-frequency capacitance, the relaxation phenomena, and the leakage current [4]. In opposite to the voltage-step technique a discrimination between varistor-type effects and long term degradation of the leakage current is not possible in a single experiment, since voltage and time are coupled. The main disadvantage of the voltage-ramp stimulation is that the high-frequency capacitance is charged with a constant rate during the whole measurement. This charging current may superimpose important features of the relaxation and leakage currents as will be shown in Section 4.

3. Electrical equivalent circuit

The calculation of electrical signal responses of thin films requires an adequate electrical equivalent circuit. If a simple network consisting of passive elements is used, one has to keep in mind that this model can only represent time independent and linear systems. Perovskite-type dielectric thin films usually follow the Curie-von Schweidler law, i.e. a t^{-n} decay of the current with time, where the coefficient is in the range of approx. $0.4 \leqq n \leqq 1$ [1][5]. This law of the current can be represented as a superposition of Debye-type relaxations without making assumptions about the physical background [6]. Further features that have to be covered by the electrical equivalent circuit concern the high-frequency capacitance, determined by the capacitor's geometry and the high-frequency dielectric constant, on the one hand and the leakage current on the other hand. The resulting equivalent circuit is shown in Fig. 1 together with a voltage source and an amperemeter which cause the unavoidable system resistances combined in R_s.

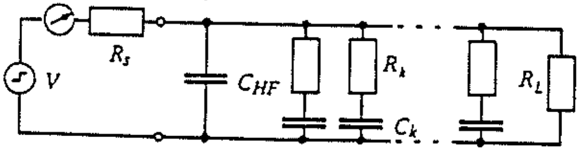


Fig. 1: Electrical equivalent circuit for perovskite-type dielectric thin films consisting of a finite number of RC-elements R_kC_k, a parallel leakage resistance R_L and a high-frequency capacitance C_{HF}. In addition a voltage source and an amperemeter are shown. Their resistances can be combined in the resistor R_s.

4. Simulation of relaxation and conduction

The values of the RC-elements R_k and C_k can be evaluated from the discharging current of a voltage-step experiment. If, therefore, the voltage-step response is calculated based on such an equivalent circuit, the result can state the correctness of the simulation but it reveals no new information. Fig. 2 shows a comparison between measured and calculated data.

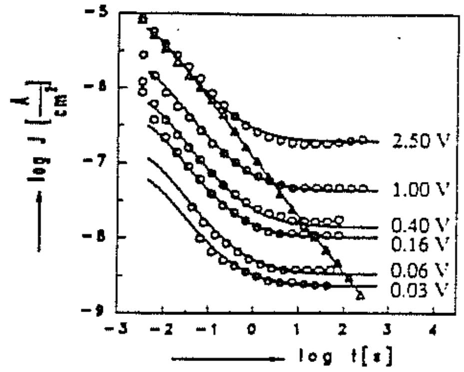


Fig. 2: Comparison between experimental voltage-step data and the calculated response. The measurement was carried out on a La-doped $SrTiO_3$ thin film (thickness 180 nm, contact area 1 mm^2) at a temperature of 425 K.

Very instructive is the simulation of voltage-ramp experiments with varying ramp slopes. In Fig. 3, calculated current responses to voltage-ramps of three different slopes are given. Experimental data from voltage-step responses, accomplished at a temperature of 425 K, are also included into the lg J vs. lg E plot. The ohmic low-field regime was not covered in this specific measurement. Therefore, it is just indicated by a dashed line as known from comparable studies.

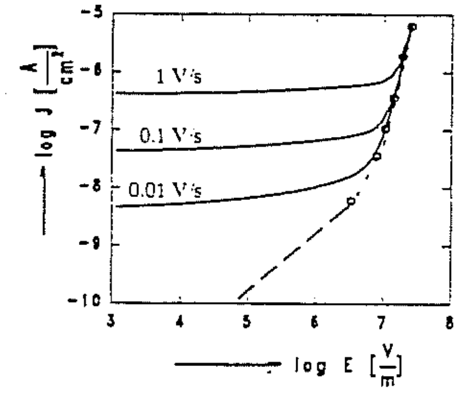


Fig. 3: Calculated current density - field characteristic like it would result from voltage-ramp experiments (solid lines). The simulation is based on a thin film equivalent circuit including the high-frequency capacitance and the system's resistances. Up to relatively high fields the ramp-test data are not comparable to experimental data from voltage-step responses (circles).

The current responses to the voltage-ramps are clearly dominated by a constant current up to relatively high fields. This current

$$I = C_{HF} \cdot \frac{dV}{dt} \neq f(t) \qquad (1)$$

is determined by the high-frequency capacitance and the slope of the ramp. The calculations show that even moderate ramp slopes of 0.1 V/s cause big errors in measuring leakage currents at small electrical fields. This comparison of the ramp response with the real leakage data clearly demonstrates the advantage of the voltage-step technique. While the voltage-step instantly charges the high-frequency capacitance, so that it does not give rise to a current contribution for times $t > R_S C_{HF}$ ($\approx$240 ns in the described example), the current response in the ramp-technique carries a constant offset due to the sustained charging of C_{HF}.

5. Conduction regime

In this Section, results for the influence of the electrode contact materials on the leakage current are presented. A variety of different materials have been employed as top electrode contacts for this study [2]. In all cases the bottom electrode was Pt. In the case of a Pt cathode the leakage currents are low and equal, independent of Pt being the top or bottom electrode. In the case of other cathode materials, for example Au or Al, higher leakage currents are observed. This result unequivocally shows that only the cathode determines the leakage behaviour of titanate thin films. The polarization and depolarization currents are found to be independent of the polarity and the electrode metals. In Fig. 4, the lg J vs. lg t curves for some cathode materials are presented.

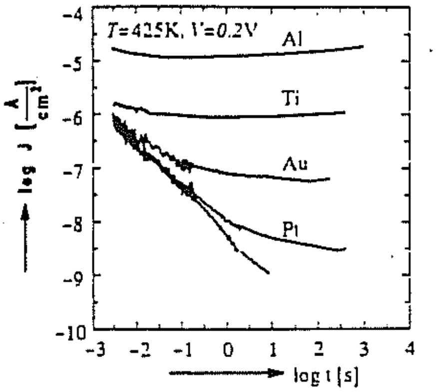


Fig. 4: Current density J vs. time t for 0.1 at% Ni-doped SrTiO₃ films at 425 K and 0.2 V. Comparison of different top electrode materials as cathodes. All films have Pt bottom electrodes.
Film thickness: 230 nm
Only one representative depolarization current curve is shown, because these curves are the same within the experimental scatter.

Because the leakage current is clearly dominated by the cathode electrode interface, it can not be explained by a bulk effect like space-charge-limited currents or the Poole-Frenkel effect. The temperature dependence of the leakage current supports the model of thermionic emission of electrons from the cathode electrode which leads to the following dependence:

$$J = A^{**} \cdot T^2 \cdot \exp\left(-\frac{W_B}{kT}\right) \cdot \left[\exp\left(\frac{qV}{kT}\right)-1\right] \qquad (2)$$

where J is the current density, A^{**} the effective Richardson constant, T the absolute temperature, W_B the height of the energy barrier, and V the applied voltage. The barrier height W_B in general is voltage dependent because of the Schottky effect [7]. For checking the thermionic emmission, Fig. 5a) comprises the results for different metals in a $\ln(J/T^2)$ vs. 1000/T plot according to Eq. (2). The curves unequivocally show the dependence anticipated for a thermionic emission. The barrier height W_B can be calculated from the slopes of the curves using Eq. (2).

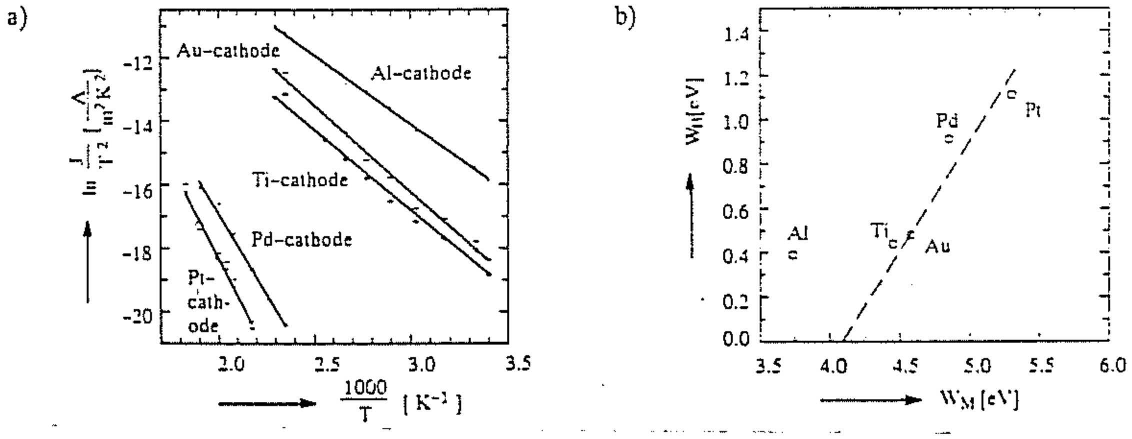


Fig. 5: a) Temperature dependence of the leakage current density for 0.1 at% Ni-doped SrTiO₃ films. Al, Au, and Ti cathodes: film thickness = 370 nm, voltage = 1.26 V; Pt cathode: film thickness = 230 nm, voltage = 1.0 V; Pd cathode: film thickness = 460 nm, voltage = 1.57 V
b) Barrier heigth W_B at the cathode contact of Ni-doped SrTiO₃ films vs. the work function W_M of the cathode metal.

As shown in Fig. 5b) there is a reasonable correlation of the barrier height W_B with the workfunctions W_M with the exception of Al. This exception is plausible because the workfunction of Al is smaller than the electron affinity of $SrTiO_3$ and, therefore, other mechanisms than the Schottky-effect may be dominant. Moreover, in judging the results one has to keep in mind that surface-states may decrease the slope of the line inserted into Fig. 5b).

6. Breakdown

Breakdown experiments have been performed, ramping the voltage up with different ramp slopes until the capacitor suddenly loses its insulating properties. The current-flow before the breakdown occured and the moment of the breakdown itself have been observed. Fig. 6 shows typical results with a time resolution of 20 ns between two vertical lines.

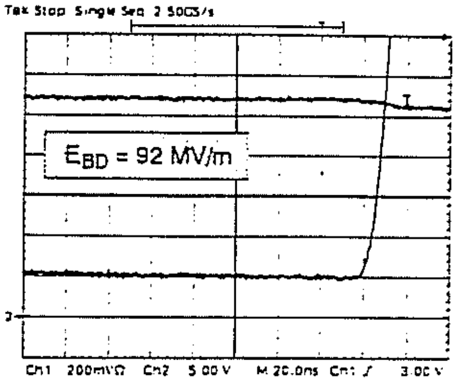


Fig. 6: Breakdown of a 0.1 at% Ni-doped $SrTiO_3$ film (thickness: 300 nm).
Upper curve: voltage drop over the sample (5V / spacing)
Lower curve: current through the sample (2 μA / spacing)
Slope of the voltage-ramp: 0.1 V/s.

The upper curve represents the voltage drop over the sample. The scaling is 5V per spacing, yielding a breakdown voltage V_{BD} = 27.5 V. The lower curve represents the current through the sample which is approx. 200 μA before the breakdown occures. The voltage-ramp in Fig. 6 was 0.1 V/s. The results remain nearly unchanged if a slope of 3000 V/s is adapted. These first results show that the breakdown is unlikely to be of a thermal runaway type because it occurs very abruptly. Furthermore the accumulated charge or a pre-breakdown degradation cannot be critical because the pre-breakdown current and the breakdown field remain the same even for orders of magnitude different ramp-slopes.

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Short report on the activity of EPFL/LC in COST 514 project: "Reliability of ferroelectric thin films"

Author: A.L.Kholkine

Problem:

Ferroelectric thin films are very promising for applications in microelectromechanical systems because of their large piezoelectric coefficients and high breakdown fields. However, very little is known about the degradation mechanisms of electromechanical properties which determine the long-time behaviour of thin film devices. Even the values of piezoelectric coefficients are unknown for most of the ferroelectric films. It is the goal of this project to characterize the piezoelectric and other electromechanical properties of ferroelectric thin films and to find out the nature of electromechanical degradation which can limit their use in different applications.

Results:

1. The experimental set-up has been developed on the base of Michelson-Morley optical interferometer which is able to measure the displacements in the range $2\ 10^{-4}$-10 nm over the frequencies 0.5-100 kHz. The key issues are the short optical length between two arms which reduces the thermal drift and beam divergence and the rigid mounting of optical and mechanical components which prevents the mechanical resonances. The stabilization of interferometer is achieved by introducing the feedback system which maintains the interferometer in the most sensitive $\lambda/4$ position by driving the reference mirror. The system was tested by measuring the displacements in standard x-cut quartz samples (Fig.1). The system showed a good stability sufficient for long-time degradation experiments.
2. The measurements of electric field-induced displacements in PZT films have been carried out. They showed the large contribution of bending vibrations in the system substrate-bottom electrode-PZT film-top electrode (bimorph behaviour) which prevents the study of true piezoelectric response. The bending effects were significantly reduced by proper clamping of the substrate to a rigid holder. The values of measured longitudinal piezoelectric coefficients lie in the range 50-150 pC/N depending on the thickness and quality of thin films and are much lower than that of bulk materials for the same composition. These discrepancies are explained by clamping the film by the substrate and by stresses developed during the film deposition.
3. The first degradation tests have been made such as ageing and fatigue under bipolar cycling. The large influence of poling conditions on ageing is found. The loss of piezoelectric properties with time reveals the initial fast component and rather slower logarithmic decay at longer times (Fig.2). The degradation under bipolar cycling showed the large asymmetry of piezoelectric response in the initial stage (Fig.3) which may be caused by locking of the domain walls by the charges trapped near the metal-electrode interface. In this state some improvement of piezoelectric properties at zero field have been observed. The further cycling restores the symmetry of piezoelectric response and results in the decrease of piezoelectric coefficients. The degradation test with PZT films deposited on thin Si membranes showed no significant changes in resonance frequencies and amplitudes of the vibrations during 100 h of operation imitating the work of piezoelectric ultrasonic motor (Fig.4).

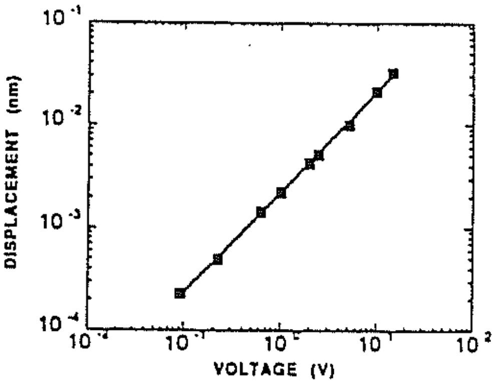


Fig.1. Displacements vs. driving voltage for quartz showing the resolution of inerferometer.

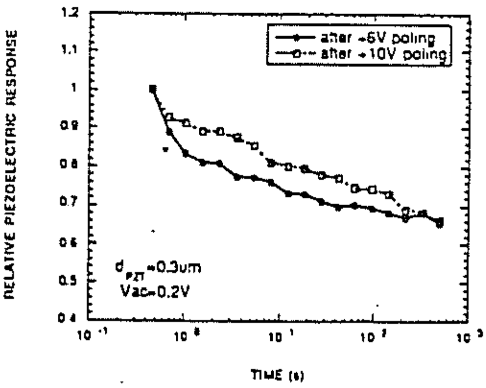
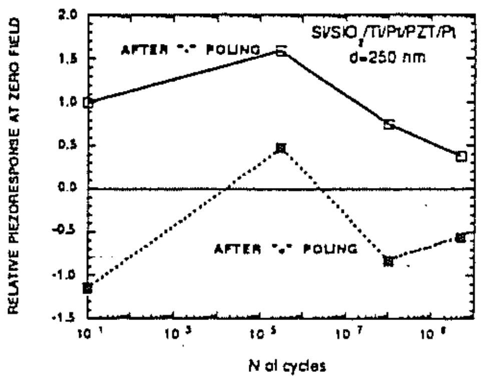


Fig.2. Typical time behaviour of piezoelectric response after poling of PZT films.



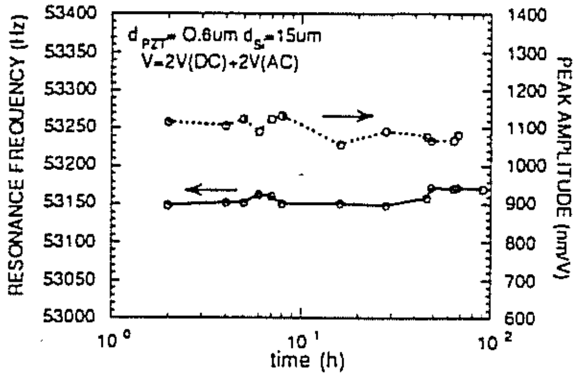


Fig.3. Degradation of piezoelectric response under bipolar cycling showing the large assymetry after 10^5 pulses.

Fig.4. Degradation behaviour of membrane imitating the work of piezoelectric motor

COST 514 EPFL/LC Collaboration with Lulea Univ. of Techn., Lulea, Sweden

K.G. Brooks, EPFL/ T. Lindback, Lulea

Investigation of Sol-Gel PZT Crystallization Kinetics by High Temperature XRD

The objective of these ongoing investigations is to try to quantitatively determine the activation energies for the crystallization of both pyrochlore i.e. the conversion of the amorphous sol material to pyrochlore, and likewise the activation energy of the subsequent pyrochlore to perovskite conversion. At first, a single substrate system is to be studied (i.e. $Si/SiO_2/TiO_2/Pt$). Based on the results of these studies, perhaps other bilayer metallizations, e.g. Ta/Pt, or other substrate materials. The collaboration to date consisted of the preparation of approximately 20 PZT films, of such a size as to be compatible with the high temperature XRD equipment at Lulea. Two sets of films were prepared by K. Brooks at EPFL. The first set is of PZT 53/47 composition which has been crystallized by RTA (650°C/10 min.). These are being used as standards to compare with the second set of films which will be crystallized in-situ in the high temperature XRD at Lulea. The second set of films was prepared by sol-gel deposition followed by a pyrolysis treatment at 350°C for 15 s. No further heat treatments were carried out.

COST 514 EPFL/LC Collaboration with RWTH, Aachen, Germany

A.L.Kholkine, A.K.Tagantsev EPFL/ R.Waser, G.Dietz, RWTH

Investigation of DC conduction and Thermally Stimulated Currents in Ferroelectric and Non-Ferroelectric Thin Films

The goal of this study is to investigate the mechanisms of DC conduction and dielectric polarization in ferroelectric (PZT) and non ferroelectric ($SrTiO_3$) films and the influence of impurities on these processes. The comparison of both materials as well as the thin films and bulk ceramics will allow to make the definite conclusions about the nature of impurity states, the influence of ferroelectric polarization on DC conduction, the role of microstructure in the conduction and polarization processes. At this initial stage of research, the samples and the measurements technique are under the preperation.

PULSED LASER ABLATION DEPOSITION OF FERROELECTRIC CERAMIC THIN FILMS

-a COST Action 514 Project

a brief summary of activities in 1994

Aim of the study

This project is to study in depth the Pulsed Laser Ablation technique in producing ferroelectric and conducting (electrode) oxide materials with following participants:

Prof. K. V. Rao	Royal Institute of Technology. Department of Condensed Matter Physics. Stockholm. Sweden
Prof. Seppo Leppävuori	University of Oulu.Microelectronics and Material Physics Laboratories. Oulu. Finland
Dr. A. E. Hill	University of Salford. Department of Electronic and Electrical Engineering. Salford. U.K.
Prof. I. Boyd	University College London. Department of Electronic and Electrical Engineering. London. U.K.

Materials and processess studied

Pulsed laser ablation deposition of PZT and other ferroelectric oxides and conducting oxide electrodes (includig high Tc superconductors) and their heterostructures has been studied. and the structure and properties of the films and heterostructures have been characterized. Different types of laser were used for the deposition. The properties of laser plume and depositing particle beam were studied. The scientific activities of each partner are briefly stated as follows.

Royal Institute of Technology. Stockholm (KTH)

- Using Nd:YAG laser (frequency tripled $\lambda = 355$ nm) the feasibility to produce ferroelectric/ superconductor PZT/YBCO bilayers and YBCO/PZT/YBCO trilayers in situ on single crystal $LaAlO_3$ was demonstrated. A linear dielectric constant of 620 for PZT with dissipation factor of $\tan\delta=0.1$ at 1kHZ. a remnant polarisation of 29 $\mu C/cm^2$. and coercive fields in the range of 70 - 85 kV/cm were obtained. The thinness dependence of of basic parameters of PZT relevant for non-volatile memory applications was investigated. Thinnest PZT film (30 nm) with good characteristics was investigated and produced.
- $PbTiO_3$/YBCO heterostructures with almost square hysteresis loops with high remanent polarisation values of 60 uC/cm^2, low dielectric constant of 90 along the c-axis and $\tan\delta$ values of 0.03 were produced.
- New thin material ($PbSc_{0.5}Ta_{0.5}O_{0.5}$) of interest for pyroelectric sensor application was identified.
- Studied fundamental problems of laser plume and its structure.
- Developed new capabilities to deposit multilayers by computerizing the PLD system.
- Explored the field effect properties of HTSC/PZT structures.

University of Oulu

– Layered thin film structures containing Nd doped PZT and conducting lanthanum strontium cobalt oxide (LSCO) or high Tc superconducting $YBa_2Cu_3O_{7-\delta}$ (YBCO) compound were deposited on $SrTiO_3$ and MgO in an *in situ* process by pulsed laser ablation using an XeCl excimer laser (λ =308 nm). For some structures, laser ablated Pt top electrodes were used. For the best films, the maximum polarization at an electric field of 400 kV/cm was 30 $\mu C/cm^2$, the remanent polarization was 18 $\mu C/cm^2$ and the coercive field about 80 kV/cm.
– The structure, orientation relationships and degree of epitaxy and crystal perfection of the films were studied by XRD, SEM and micro-Raman specroscopy. Good crystal perfection, phase purity and epitaxy of PZT was obtained on STO substrates and on c-axis oriented epitaxial YBCO films deposited on STO substrates and on epitaxial LSCO deposited on STO and MgO. The PZT target composition was reproduced well in the films.
– Studies of post-annealed polycrystalline PZT films has been continued. Generally, in situ grown films had higher polarization but lower resistivity.
– Experiments has been started to deposit PZT on epitaxial laser ablated yttrium-stabilized zirconia (YSZ) buffer layers on Si (100) and silicon-on-sapphire (SOS).
– As an application of YBCO/PZT heterostructure, a superconducting, current controllable, distributed RC-component was designed and fabricated. In this application the PZT film acted as a passive high ε material.

University of Salford

– Main activity in the COST program has been in completing the construction of the laser ablation deposition facility, introducing modifications such as an oxcygen bleed to accommodate PZT material and initial preparation of PZT films from a target supplied by the oulu group. The films are presently being analysed and the optimum conditions of substrate temperature, oxygen partial pressure and post deposition annealiung/ sintering are being establised.
– High powered Lamda-Physik 205i excimer laser has been installed. A range of gas mixtures are available allowing ablation at various wavelegths, but XeCl (λ = 308 nm) has been adopted as standard.

University College London (UCL)

– PZT film were deposited on MgO substrates using both frequency doubled (532 nm) and quadrupled (266 nm) Nd:YAG laser. Preliminary depositions using KrF excimer laser (248 nm) have also been performed As-deposited films were analysed using XRD, EDX, EPMA and RBS. Optimised ablation conditions (Tsub = 560°C, p_{O_2} = 0.25 mbar) yielded (001) oriented PZT. Films were generally free of droplet contamination, most notably when UV ablation employed.
– Current deposition studies include the use of ozone and N_2O as oxidant species. Multilayer structures of PZT/YBCO/MgO and PZT/Pt/MgO are also being deposited.
– Kinetic energy distributions of the ions in laser-induced plasma have been measured using a linear combination of modified cylinrical mirror analyser (CMA) and a quadrupole mass spectrometer (QMS). In vacuum (10^{-7}) Pb^+, Ti^+, Zr^+, ZrO^+ and O^- were the main ionic plume constituents. At laser fluences around 1 J/cm^2 the ion energy was distributed between 25 - 40

eV. At higher fluences, high energy ions (50 - 200 eV) were detected. At high ambient gas pressures (p_{O_2} 10^{-3} mbar) the ion signal decreases rapidly and the ions undergo collisions leading to lower energies.

Cooperation and connections

- Prof. Rao has organized a workshop on Ferroelectrics with about 75 participants at KTH.
- Members of Oulu group have made 2 visits to KTH. Collaboration was planned.
- Dr. Hill (Salford) has visited Oulu.
- Oulu group has submitted PZT targets to Salford.
- An application for student exchange program under ERASMUS with Dr. Hill as coordinator has been submitted.
- KTH has established contact with research group at Univ of Latvia, Riga, and exchange of researchers and samples, and initiated a new project on studies of dynamics of the plume during pulsed laser deposition of ferroelectric materials.
- The programme of Salford group has been expanded to include joint work with the computer storage group of the University of Manchester, who are using PZT linear actuators to read digital information stored on magnetic media. Instead of their present commercial actuators they wish to use devices based on thin films.

Microelectronics and Material Physics Laboratories. University of Oulu.
PL 400, FIN-90571 Oulu, Finland.

COST 514 Program	Report of activities in 1994
Title of the project	Pulsed laser ablation deposition of ferroelectric thin films
Principal Investigator	Prof. S. Leppävuori
Group members	J. Levoska, J. Lappalainen, T.Murtoniemi, J. Frantti

Summary

Pulsed laser ablation deposition of PZT and conducting oxide electrodes (includig high Tc superconductors) and their heterostructures by an *in situ* process has been studied, and the structure and properties of the films and heterostructures have been characterized. Our earlier studies of post-annealed polycrystalline PZT films has been continued.

Scientific results

Layered thin film structures containing ferroelectric Nd doped lead zirconate titanate (PZT) and conducting lanthanum strontium cobalt oxide (LSCO) or high Tc superconducting $YBa_2Cu_3O_{7-d}$ (YBCO) compound were deposited in an *in situ* process by pulsed laser ablation using an XeCl excimer laser and sintered polycrystalline targets. The structures were grown on heated strontium titanate (STO) (100) and MgO (100) single crystal substrates. Experiments has been started to deposit PZT epitaxial laser ablated yttrium-stabilized zirconia (YSZ) buffer layers on Si (100) and silicon-on-sapphire (SOS).

The structure, orientation relationships and degree of epitaxy and crystal perfection of the films were studied by X-ray diffraction, scanning electron microscopy (SEM) and micro-Raman specroscopy. Good crystal perfection, phase purity and epitaxy of PZT was obtained on STO substrates and on c-axis oriented epitaxial YBCO films deposited on STO substrates and on epitaxial LSCO deposited on STO and MgO. The PZT target composition was reproduced well in the films. It was found that the substrate has an effect, not only on the orientation and possible epitaxy, but also on the formation of different phases in the PZT system.

Capacitor structures were were fabricated using masking during the deposition. For some capacitors, laser ablated Pt top electrodes were used. Ferroelectric properties of PZT films and resistive properties of the structures were measured both at room temperature and cryogenic temperatures. For the best films, the maximum polarization at an electric field of 400 kV/cm was 30 $\mu C/cm^2$, the remanent polarization was 18 $\mu C/cm^2$. Generally, in situ grown films had higher polarization but lower resistivity.

As an application of YBCO/PZT heterostructure, a superconducting, current controllable, distributed RC-component was designed and fabricated. In this application the PZT film acted as a passive high ε material. The component consisted of a YBCO thin film resistor, which was covered with a dielectric layer and an electrode to form a capacitor. The YBCO thin film was deposited by pulsed excimer laser ablation on a $SrTiO_3$ (100) substrate. It was patterned by photolithography and wet etched to form a meandering type tapered strip. This YBCO strip was covered with a lead zirconate titanate (PZT) layer made by laser ablation and, finally, the dielectric layer was covered with a gold electrode by vacuum evaporation. The electrical characteristics of the superconducting YBCO film and the RC-component were measured. Using the constructed component, high-pass and notch filter circuits were demonstrated. It was possible to control the electrical properties of these filters by a dc-current applied through the YBCO strip which causes the superconducting film to become partly resistive.

Publications

J. Levoska, S. Leppävuori, T. Murtoniemi, J. Lappalainen. Laser ablation deposition of ferroelectric lead zirconate titanate and high Tc superconducting Y-Ba-Cu-O layers. Prodeedings of Electroceramics IV, 4th International Conference on Electronic Ceramics & Applications, September 5 - 7, 1994, Aachen, Germany, 339-342.

J. Frantti , V. Lantto. Characterization of $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$ thin films prepared by laser ablation, Journal of Applied Physics, 76 (1994) 2139-2143.

J. Lappalainen, J. Frantti, S. Leppävuori, Characterization of post-annealed PZT thin films deposited using pulsed laser ablation, accepted to Mat. Res.Soc. Symp. Proc.

J. Hagberg, J. Levoska, S. Leppävuori, T. Murtoniemi, Y-Ba-Cu-O/PZT distributed RC-element, accepted to Mat. Res. Soc. Symp. Proc.

COST 514 - Salford University, UK

Summary

The main activity in the COST program has been in completing the construction of the laser abla deposition facility, introducing modifications such as an oxygen bleed to accommodate PZT mate and in initial preparation of PZT films from a target supplied by the Oulu group. The programme also been expanded to include joint work with the computer storage group of the University Manchester.

Equipment

The basic layout of the facility is shown in Figure 1. The high powered Lamda-Physik 205i exci laser is installed in a separate room together with its gas cabinet. A range of gas mixtures are availa allowing processing to be performed at various wavelengths, but the gas mixture XeCl has b adopted as standard to give compatibility with other members of the group. The details of the la are given in Appendix 1.

The working chamber consists of a turbo-molecular pumped stainless steel chamber with a b pressure less than 10^{-6}mbar. The laser beam is pre-focused outside the chamber and enters via a qua window which is situated remote from the deposition area in order to minimise contamination of window by the evaporant.
The beam focus is at the surface of the target which has an area of ~1cm² and is held at an angle 45° to the beam. The beam remains fixed while the target is moved by stepping motors and a comp mechanical coupling to produce independent movement in X, Y and Z directions. X and Y movem allow the surface of the target to be scanned in any desired pattern while the Z movement is used provide automatic height compensation to avoid defocusing during movement in the Y direction. T whole system, including control of the laser pulse firing, is under the command of a dedica computer. The system is illustrated in Figure 2.

The raster pattern adopted for the PZT depositions is shown in the inset of Figure 1. The laser focused to give a relatively broad, rectangular spot measuring approximately 3mm by 1mm. This rastered repeatedly over the target surface to give an ablated area of 9mm square. The substrates ha initially been of glass but more suitable materials will be substituted after the initial phase has be completed. The substrate holder, which may be heated to 500°C, is rigidly connected to the targ assembly and is separated from it by a distance of 4cm. Deposition of films from t $Pb_{0.97}Nd_{0.02}(Zn_{0.55}Ti_{0.45})O_3$ was performed in an oxygen partial pressure of 200μbar.

The films are presently being analysed and the optimum conditions of substrate temperature, oxyg partial pressure and post-deposition annealing/sintering are being established.

Co-operation within COST with the University of Manchester

As a direct result of Salford's participation in the COST 514 programme, a new co-operation has bee initiated between the Salford group and the computer storage group of the Department of Electric Engineering of the University of Manchester. They are currently using PZT linear actuators to rea digital information stored on magnetic media. Instead of their present commercial actuators they wis to use devices based on thin films. Some initial joint work is currently proceeding to evaluate lase ablated PZT films made on the Salford facility with a view to fabrication of a prototype device.

A E Hi
R D Pilkingto

INVESTIGATION OF PULSED LASER DEPOSITION OF LEAD ZIRCONATE TITANATE THIN FILMS

Department of Electronic and Electrical Engineering, University College London,
Torrington Place, London, WC1E 7JE, England, United Kingdom

The use of lead zirconate titanate (PZT) is now widespead as a possible ferroelectric material for use in devices such as non-volatile random access memories. Pulsed laser deposition (PLD) has been for several years proposed as a particularly effective method of thin film fabrication for perovskite-based materials because of the congruent transfer of target material to the growing film without significant loss of volatile components. This project can be conveniently divided into two components. Firstly, this study addresses the salient features of optimised film deposition and secondly investigates the important aspect of congruent transfer by reference to energy-dispersive mass spectrometric measurements..

PLD OF LEAD ZIRCONATE TITANATE THIN FILMS

PZT films were deposited on MgO (100) substrates using both frequency doubled (532nm) and quadrupled (266nm) Nd:YAG laser radiation (4ns pulse duration). Preliminary depositions using 248nm KrF excimer radiation (20ns pulse duration) have also been performed. The target pellets were hot-pressed, and showed a stoichiometry of $Pb(Zr_{0.54}Ti_{0.46})O_3$. In addition, additives such as Sr, Nb and Al_2O_3 were present in small quantities (total <2%). These primarily control grain boundary properties. The targets were found to be well preserved after many thousands of laser pulses. Discolouration of the laser irradiated pellet was due to cone formation on the surface. By employing the multiple ion monitoring technique over an several hours it was found that plume constituents remained constant, thus indicating that target stoichiometry remained constant. EPMA of the target material verified this observation.

Typical laser fluences for deposition were in the range 4-12 J/cm^2. Lower fluences (1-2 J/cm^2) were used with uv laser radiation As-deposited thin films were analysed using XRD, EDX, EPMA and RBS. Optimum conditions were found to exist at T_{sub} 560°C and pO_2 0.25 mbar. The target -substrate distance was optimised at 40mm and the substrate was heated using a quartz lamp heating system. The film morphology, as determined by electron microscopy, was found to be good. The thin films were generally free of droplet contamination, most notably when uv ablation was employed.

The optimised abaltion conditions yielded PZT (00l) XRD reflections of which the (001) and (002) peaks were most intense. By decreasing the pO_2 the lattice parameter could be slightly influence and thus lattice parameters form 4.07Å to 4.10Å were measured. The FWHM of the (001) peak was typically around 0.2° thus indicating very good preferred orientation.

Current deposition studies within this programme include the use of ozone and N_2O as oxidant species. Multilayer structures of PZT/YBCO/MgO and PZT/Pt/MgO are also being deposited.

ENERGY-DISPERSIVE MASS SPECTROMETRIC ANALYSIS OF THE LASER-INDUCED PLASMA

The kinetic energy distributions of the plume constituents have been measured using a linear combination of modified-cylindrical mirror analyser (CMA) and quadrupole mass spectrometer (QMS). Our system can detect ion masses up to 600 a.m.u. and ion energies between 0-500eV. Thus far, we have concentrated our studies on measurement of ions within the laser-induced plasma.

Mass spectral studies in vacuum (10^{-7} mbar) reveal the presence of Pb^+, Ti^+, Zr^+, ZrO^+ and O^+ as the major ionic plume constituents. At laser fluences around 1 J/cm^2 the ion energy is distributed between 25-40 eV. At higher laser fluences, high energy ions (50-200eV) are detected. At high ambient gas pressures (pO_2 10^{-3}mbar) the ion signal decreases rapidly and the ions undergo collisions leading to lower energies. Extrapolation to typical deposition temperatures reveals almost complete thermalisation of ionic species within the plasma front. Monte Carlo simulations of these conditions shows reasonable agreement with these observations.

The ion emission at low fluences (< 1 J/cm2) is also currently being investigated in order fully characterise the ablation mechanisms for this material. It is observed that ions are detected at laser fluences below where a laser-induced plasma is seen. These studies are not complete at the present time.

COST 514 Program — Scientific report
(For the period Jan - Dec 1994)

Title of the project — Pulsed laser ablation deposition of ferroelectric thin films

Principal Investigator
Prof. K. V. Rao
Dept of Condensed Matter Physics
Royal Institute of Technology
S-100 44 Stockholm, Sweden

Group members:
Dr. A.M. Grishin, C. Björmander, Dr. K. Sreenivas, and
Dr. M. A. Tyunina

The recent widespread resurgence of interest in ferroelectric thin films has been mainly motivated by the potential for applications in non volatile memories, pyroelectric imaging arrays, and miniaturised micro actuators. Availability of thin films makes it possible to operate ferroelectric materials at low and practical levels of voltages in microelectronics circuitry. It has become increasingly evident that optimum use requires close control of film structure and orientation, and understand the strongly anisotropic properties of ferroelectrics. The need arises primarily to develop reproducible film deposition technologies, understand the dimensionality effects in thin ferroelectric films, and develop novel heterostructures for improved functional performance. The pulsed laser deposition (PLD) technique has been particularly a focus of interest, as it is a fast and a versatile process capable of producing stoichiometric films of multicomponent oxides. This report summarizes the work completed at the end of the first year of this project. The research was directed towards a better understanding of the laser deposition process and properties of ferroelectric/superconductor heterostructures.

We have recently demonstrated that with a much more inexpensive operation using a Nd:YAG laser, high quality heterostructures could be fabricated. Besides Nd:YAG laser is found to be stable, economical in maintenance, easy to control, and is environmentally safe from an industrial point of view. Using Nd:YAG laser for the first time, we demonstrated the feasibility to produce ferroelectric/superconductor PZT/YBCO bilayers, and YBCO/PZT/YBCO trilayers in-situ on single crystal $LaAlO_3$ substrates.

Mechanisms controlling the kinetics of film growth in a pulsed laser ablation technique were studied as a function of oxygen pressure with special emphasis on ferroelectric $Pb(Zr,Ti)O_3$ films. Film thickness distribution profiles demonstrated a good fit to the model of adiabatic expansion of the plasma plume. Increase of growth rate with increase in oxygen pressure was observed without narrowing of plasma plume. Different modes of increase in the growth rate observed as a function of distance from the center of the plume were conceived due to the angular distribution of an anisotropic distribution of particle flow in the plasma plume.

In the PZT/YBCO heterostructures a sharp superconducting transition at 89.5K with a width of δTc=1K is observed for the underlying YBCO thin films. A linear dielectric constant of 620 for PZT with a dissipation factor of (tanδ=0.1) at 1 kHz, a remnant polarisation value of 29 μC/cm^2, and coercive fields in the range of 70-85 kV/cm are obtained. These results have been reported in the Appl. Phys. Letters, June 27, 1994 issue.

These epitaxial device structures consisting of conducting oxides such as YBCO are attractive because they provide coherent contacts between the electrodes and the ferroelectric layers, due to good structural, and chemical compatibility. Coexistence of such good superconducting and ferroelectric properties are promising for a variety of electronic device applications combining high dielectric constant ferroelectric films and superconducting oxides.

Figure 1 shows the excellent growth of ferroelectric layers as thin as 20 nm with good reproducibility in structural properties. Recently we have reported for the first time on the thickness (d) dependence of the coercive electric field E_C of highly c-axis oriented niobium (Nb) doped PZT films over an extended thickness range of 0.06 to 1.05 μm. The observed thickness dependence of the coercive field ($E_C \sim d^{-2/3}$) as shown in fig.2 is found to be in good agreement with the domain nucleation model developed for ferroelectric single crystals by Kay and Dunn, and are in contrast to earlier reports on polycrystalline PZT thin films. These results have been accepted for publication in the Applied Physics Letter journal, Feb. 1995. Thus the ability to grow ferroelectric layers as thin as 20 nm leads to a promising approach for creating novel ferroelectric superlattices structures.

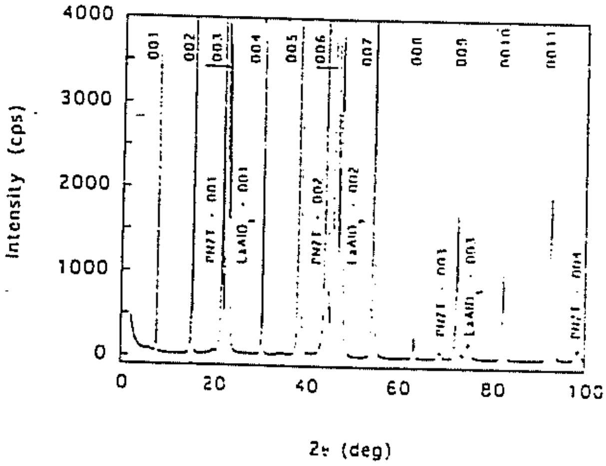


Fig.1 X-ray diffraction spectra for a 20 nm thick Nb doped PZT layer on a YBCO buffer electrode.

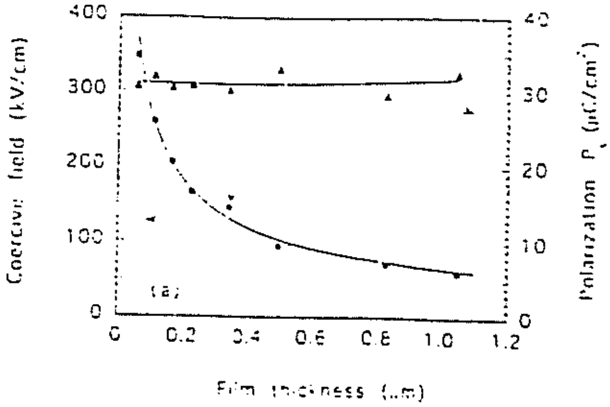


Fig.2 Thickness dependence of ferroelectric properties of Nb doped PZT thin films.

In continuation towards understanding other ferroelectric materials deposited by the laser ablation techniques, our recent efforts were focused on two strategically important materials- Lead scandium tantalate($PbSc_{0.5}Ta_{0.5})O_3$ and Lead titanate ($PbTiO_3$) well known for their pyroelectric properties. Highly c-axis oriented $PbSc_{0.5}Ta_{0.5}O_3/YBa_2Cu_3O_{7-x}$ (0.5μm/0.2μm) thin film heterostructures have been developed *in situ* on a $LaAlO_3$ substrate using a Nd:YAG pulsed laser deposition system. The ferroelectic phase transition in a 0.5 μm thick c-axis oriented $PbSc_{0.5}Ta_{0.5}O_3$ film is broadened, and suppressed to 195K with a maximum dielectric permittivity of 950, in comparison to the bulk ceramic data. The observed low loss tangent (tanδ=0.063) and the high pyroelectric coefficient $dP/dT = 4.8\times10^{-4}$ $Cm^{-2}K^{-1}$ at 195K renders $PbSc_{0.5}Ta_{0.5}O_3$ films promising for pyroelectric sensor applications. Field dependence of the reduced polarizability $\alpha E^{2/3}$over a wide temperature range (77-300K) has been found to scale with a universal behaviour as a function of $(T/T_C-1)E^{-2/3}$ This was qualitatively explained in the framework of the mean field theory. Such analysis provides an useful tool in the improvement and understanding of ferroelectric thin films.

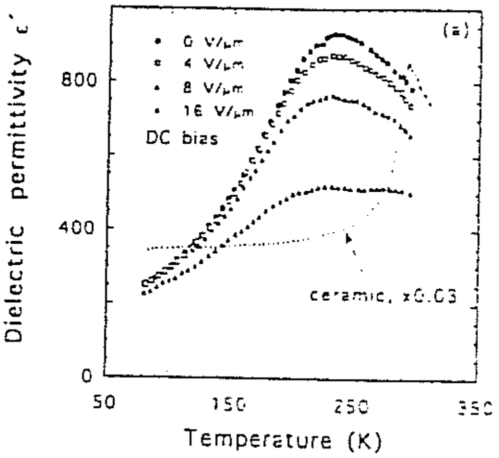


Fig.3 Dielectric permittivity versus temperature for a 0.5μm thick c-axis oriented $PbSc_{0.5}Ta_{0.5}O_3$ film

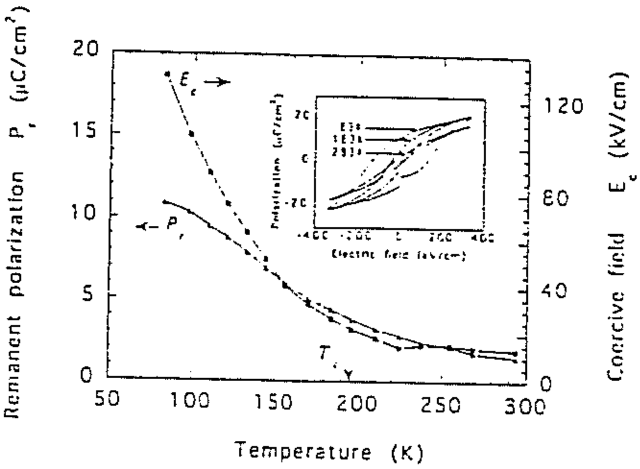


Fig.4 Temperature dependence of hysteresis loop parameters -Cu/PST/YBCO capacitor

A good lattice match between $PbTiO_3$, YBCO and $SrTiO_3$ has enabled us to produce highly crystalline c-axis oriented $PbTiO_3$/YBCO hetrerostructures with almost square hysteresis loops with high remanent polarization values of 60 μC/cm². A low dielectric constant of 90 at 1kHz and low tanδ values of 0.03 are promising for pyroelectric applications. Current efforts are focussed towards using such high quality $PbTiO_3$ films in superconducting field effect devices, and studying ferroelectric domain structures.

In the near future our plans are focused towards a better understanding of the electrode contact phenomena, dimensionality effects in thin ferroelectric films through structural and electrical characterization. Dielectric properties over a wide wide range of temperature, frequency, and applied biases, seem important to fully assess the utility of superconductor/ferroelectric heterostructures for electronic device applications.

EUROPEAN CONCERTED ACTION COST 514

PROJECT:

FERROELECTRIC CERAMIC THIN FILMS FOR SAW DEVICES

AIM OF THE PROJECT:

To obtain, by Sol-Gel and Laser Ablation techniques, and study pure and modified lead titanate ($Pb_{1-x} M_x TiO_3$, M=Ca,Sm) ferroelectric ceramic thin films suitable for use as substrates for Surface Acoustic Waves (SAW) devices.

SUMMARY OF THE PROGRESS (1994 YEAR REPORT)

A) Departamento de Materiales Ferroelectricos.
ICMM. CSIC. Serrano,144. 28006-Madrid(Spain).

Summary of presentation to workshop in following pages.

B) FERROPERM LTD. Piezoceramics Division (Denmark).
Dr. C.E. Millar Ms. W.W. Wolny

Activities:

- Advice in SAW designs at Manchester.
- Masks for photolithography for SAW devices supplied to Manchester.
- Measurements at different stages of Thin Film Processing (deposition of bottom electrode, after deposition gel film dry, thermal treatment) to determine the flatness of the substrate and films. Bending is source of strains.
- First set of ceramic targets for Laser Ablation (Sm modified lead titanate-excess lead) produced in September and supplied to CSIC.

C) Materials Science Center. Univ. of Manchester (UK).
Dr. D. A. Hall and Dr. V. Kutepova.

Activities:

- First design of 12 SAW devices : delay lines to work at $\lambda=40$, 28 and 16μm, for testing of the piezoelectric properties, and resonators to work at $\lambda=24\mu m$ and 16μm.
- Development of a suitable photolithographic method for deposition of SAW devices on first sol-gel films provided by CSIC.
- Testing of delay lines: no frequency response.
- Results of poling and testing of SAW properties in first batch of Ca-modified lead titanate thin films ready in September.

ADVANCES ON PREPARATION AND CHARACTERIZATION OF Ca MODIFIED LEAD TITANATE THIN FILMS

J. Mendiola, M. L. Calzada and L. Pardo

Instituto de Ciencia de Materiales de Madrid. CSIC.
Serrano, 144, 28005 Madrid. Spain

I.- Preparation of ferroelectric thin films

$Pb_{1-x}Ca_xTiO_3$ precursor solutions have been synthesized from a diol-based sol-gel route [1], by reflux of the following compounds:

- a diol-dissolved lead acetate trihydrate
- a solution of β-diketonate titanium alkoxide in 2-propanol
- a salt of calcium dissolved in water

With this method, an inorganic polymer is developed in solution which is responsible of the appropriate rheological parameters of the solutions for the deposition of thin films by spin coating on $Pt/TiO_2/SiO_2/(100)$ Si substrates.

Thickness of the films was controlled by the concentration, viscosity and volume of the solution deposited as well as by the spinner speed and time of deposition.

Partial elimination of organic compounds was made by drying on a hot plate at 350°C for 60 seconds.

To achieve crystallinity in the films, different thermal treatments were tested. These treatments consisted on heating at 5 and 40°C min^{-1} up to 650°C with a soaking time of 12 minutes; a rapid heating treatment consisted in bringing the furnace to the desire temperature (650°C) and stabilizing, putting the film in it, maintaining for 12 minutes, and air quenching to room temperature. These samples will be called hereinafter A, B and C, respectively.

II.- Chemical analysis and microstructure

The substrate is formed by *(1)* a (100) Si wafer, *(2)* a few nm thickness of SiO_2, *(3)* a 20 nm thickness of TiO_2 deposited by sputtering and used as antidiffusive barrier, *(4)* a 100 nm thickness of Pt as bottom electrode and *(5)* a 500 nm thickness of the ferroelectric layer $Pb_{.76}Ca_{.24}TiO_3$, deposited in a single stage by spin-on, from the synthesized solutions.

Some degree of preferred orientation along [111] has been performed on the Pt electrode after thermal annealing, but this phenomenon has not a significant effect in the possible preferred orientation of the ferroelectric layer.

Microstructures of the A, B and C samples observed by transmission and scanning electron microscopy (TEM and SEM) show a low porosity and a grain size of 120, 80 and 30 nm for each sample, respectively.

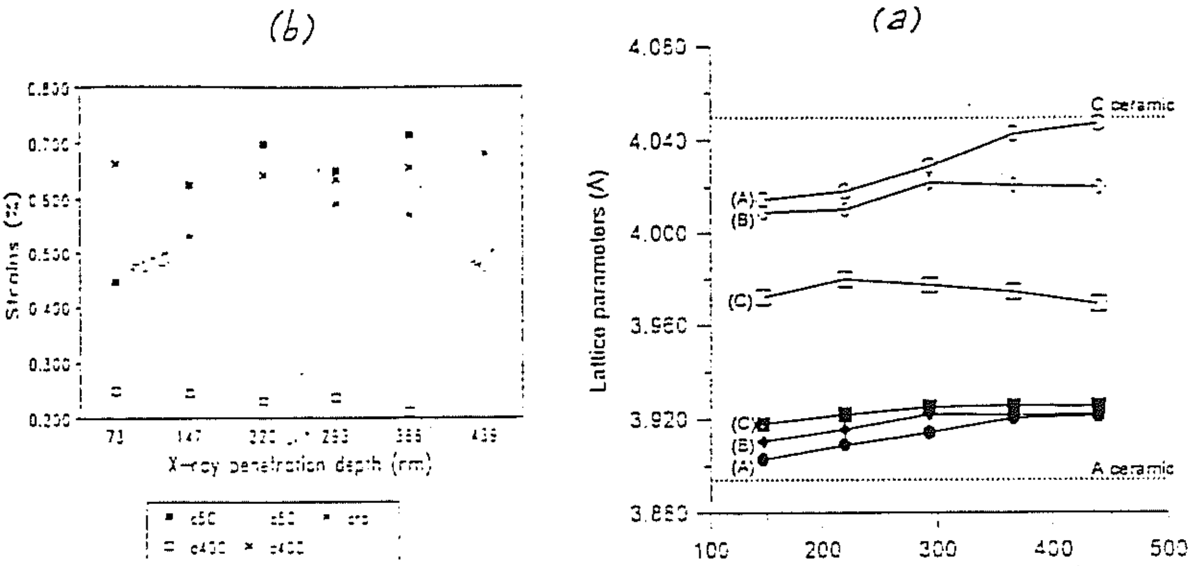


Fig. 1: a) lattice parameters variation with thickness, b) calculated strains fron XRD profiles.

A strong strained state is also deduced from gracing incident X-ray diffraction measurements (GIXRD) [2,3], especially for the sample C [Fig.1a,b], although the lattice parameters variation could be also due to a stoichiometric deviation from the nominal composition, probably as a result of the PbO losses during annealing.

By Auger and EELS analysis is observed that the Ca and Pb distribution through the thickness of the sample is not homogeneous and is dependent on thermal treatment. Thus, according with the strain results, surfaces of the films show deficiency in Pb.

The appearance of a Pb deficient pyrochlore phase is observed by GIXRD analysis, decreasing the content of this phase as the heating rate increases and being almost imperceptible in the sample C [Fig.2]. Pyrochlore content is larger close to the Pt bottom electrode that agrees with the results about Pb deficiency before mentioned and also reported by other authors for PZT thin films [4].

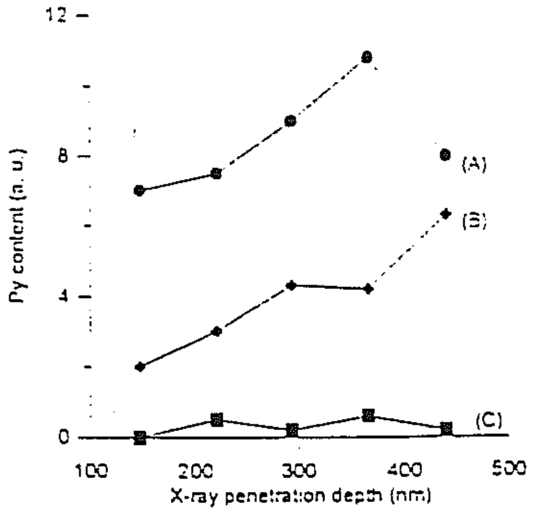


Fig.3: Pyrochlore content through the thickness of the films

III. Ferroelectric characterisation

Hysteresis loops, switching current curves and the thermal variation of the electric permitivitty measurements were performed.

The coercive field E_c of the three different samples studied here are high and the squareness of the cycles not too marked, being also very small the electric charge involved. Nevertheless, it is worthwhile to mention the results obtained when a previous electric treatment is performed. Two kinds of electric treatments have been tested before ferroelectric measurements. In the first one, a sine wave of $V_p \approx 25V$ and frequency of 1Hz was applied during 60 minutes. The hysteresis loops were taken by using also a sine wave signal V_{max} = 16V and 1Hz ; the squareness corresponding to the sample C is low compared with that of samples A and B; nevertheless, the cycles for the three samples improve and the ferroelectric charge amount increases, lowering the coercive field when compared with the samples without the electric treatment [Fig.3].

From the switching current curves, the remanent polarisation P_R and r_s have been calculated. Note the high P_R values, even 30 minutes elapsed after the electric treatment for the samples B and C [Fig.4]. The same measurements were also carried out prior the treatment; then, P_R vanished after few seconds.

A different treatment was also tested, by applying a square wave of $V_p = 16V$ and 1Hz of frequency for 60 minutes. The obtained hysteresis loops show much marked squareness, being the switching time smaller than the obtained with the sine wave treatment. On the contrary, the remanence of P_R is very small.

To summarize, the use of a previous electric treatment results very convenient to improve the ferroelectric behavior of these films, especially using a sine wave signal. Further work about the content and control of the O and Pb vacancies of these films is in progress to explain the experimental results reported here.

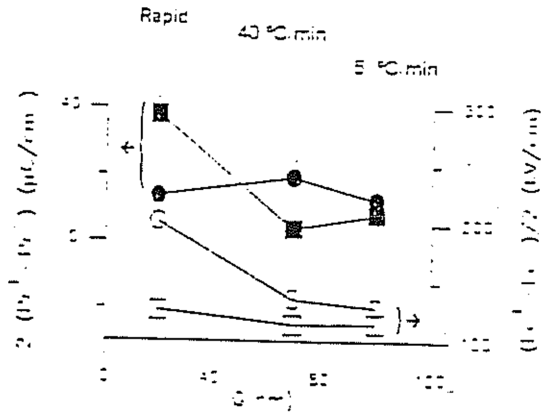


Fig.3: Thermal treatment dependence of Polarization

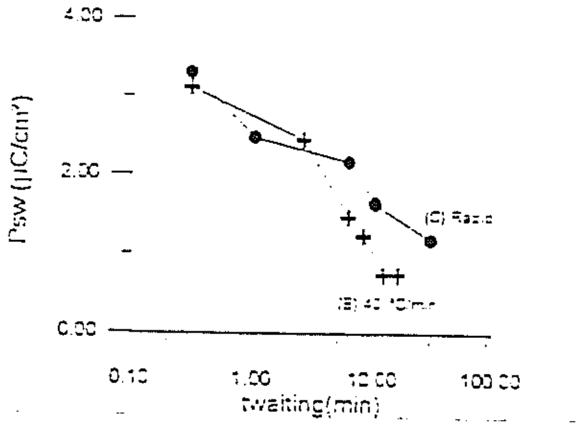


Fig.4: Psw variation with time elapsed after the electric treatment

IV.- Pulse Laser Deposition

Since a laser ablation technique has been installed in our laboratory [KrF excimer laser], we have begun the deposition of the same material. Our present work concerning with the optimization of the parameters involved in the deposition, such as partial oxygen pressure, laser fluency, target-substrate distance, substrate temperature and composition of the ceramic target. Our preliminary obtained films show low tetragonal distortion, high resistivity and low ferroelectric activity.

V.- Future work

Other substrates such as LSCO, $SrTiO_3$, MgO or Al_2O_3 will be tested, since the use of a bottom electrode seems not to be essential in SAW applications of these films.

Atmosphere will be controlled during the thermal treatments of the sol-gel-derived films as well as a much better controlled rapid heating furnace.

All of these experiments are focussed to improve the ferroelectric behavior of these films: to lower the E_c, enhance the P_R and decrease fatigue effects.

Acknowledgements

The authors would like to thank Dr. Snoeck of the CEMES-LOE [CNRS] in Toulouse-France for the HRTEM and EELS analysis and also the colaboration of all the members of the departament of Ferroelectric Materials of our Institute, especially to Dr. Carmona and Dr. Zaldo [responsible of the pulse laser deposition technique].

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European Concerted Action on Ferroelectric Ceramic Thin Films

COST 514

Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

Yearly report

February 1995

Project partners :

- IMEC, Belgium (B2)
- VITO, Belgium (B3)
- MTI, Italy (I1)
- Univ. of Pisa, Italy (I2)
- EPFL, Switzerland (CH2)

Project status

During this first year, the necessary activities for the material preparation have started at the different partners.

For the electrodes :

- Pt/Ti is studied at IMEC and MTI
- Ru and RuO2 sputtering is performed at IMEC and VITO
- laser ablation of RuO2 and LSCO is studied at University of Pisa

For the ferroelectric films :

- sol-gel PZT films are optimized both at IMEC and MTI, laser-ablated PZT is deposited at University of Pisa (a laser-ablation set-up is under construction at MTI as well).
- in the queest for Pb-free ferroelectric films, EPFL studied the deposition of LiTaO3 and SbNbO4 by sputtering

Also, some new characterization equipments were build :

- fatigue-measurement equipment at MTI
- permittivity and pyroelectric coefficient measurement equipment at EPFL
- optical multichannel analysis and in-situ mass spectrometry in Pisa laser ablation system.

Collaboration between the different partners has started by exchange of Ru/RuO2 sputtered films (made by VITO).

The first FECAPs were processed and optimized both at IMEC and MTI using Pt electrodes, as they compose a good "reference" system. This work also has given more insight in the different nucleation aspects of the PZT films The limitations of the Pt-electrode system, more specifically towards achieving the main project goal, have become apparasnt, however, and future work will concentrate more on the use of the metaloxide electrodes as RuO2.

More details about the research work can be found in the reports of the different partners in the following pages

COST 514 : Materials for a ferroelectric capacitor stack with direct contact to Silicon

IMEC activities report year 1
D.Wouters and G.Willems, February 1995

During the first year, IMEC has performed research on next two tasks :
- Study and optimization of Pt/Ti electrodes for use in sol-gel PZT FECAPs.
- Investigation of Ru as electrode material

Task 1. Study and optimization of Pt/Ti electrodes for use in sol-gel PZT FECAPs.

1.1. Bottom electrode on insulating substrate (SiO2/Si).

We have studied in detail the material interactions in the Pt/Ti bottom electrode system, the underlying SiO2/Si substrate and the sol-gel deposited PZT film, during bottom electrode anneal (before PZT deposition) and during PZT deposition and associated thermal treatments (pyrolyis and crystallization). These were investigated by SIMS, AES, RBS and XRD analysis, and also the ferroelectric properties of capacitors fabricated in this material were measured.

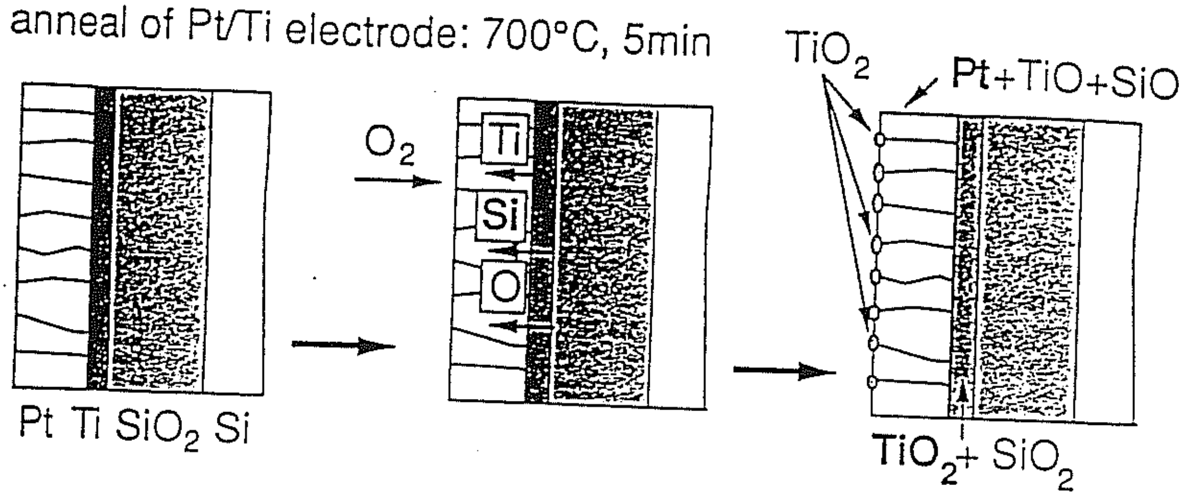
The most important factor was found to be the necessity of having (some) TiO2 present on top of the Pt before PZT deposition. This can be established by a pre-anneal in oxygen of the Pt/Ti bottom electrode sandwich structure before the PZT depositon. During that process, also some Si is incorporated in the Pt, while the Ti remaining under the Pt is fully oxidized (see Fig.1). This structure is found to be fully stabilized. During the crystallization heat treatment of the PZT film on top of this electrode structure, the TiO2 becomes dissolved resulting in PZT film enriched with Ti near this bottom electrode (see Fig.2). If no pre-anneal of the Pt/Ti electrode is performed, nucleation of the PZT is much more difficult (rosette structure is formed for MPB PZT), while we could find Si in the PZT film which migrated from the underlying SiO2 upwards during the anneal, as the structure was not stabilized.

1.2. Bottom electrode on conducting substrate

In order to investigate the possibility of making a direct contact structure using Pt electrodes, we investigated the Pt/TiN/Ti/SiO2/Si material stack for use as botom electrode material. The Pt/TiN combination (on top of polysilicon plugs) is indeed investigated for making BST (BaSrTiO) capacitors for DRAM applications with a direct bottom contact. TiN is used as conductive material since it oxidizes more slowly than Ti. However, oxygen annealing resulted in delamination of the Pt electrode film, presumably because of the large volume increase during the oxidation of TiN to TiO2 (and possible formation of N2 gas ?). So, the Pt/TiN combination seems very difficult to control and stabilize.

Study of PZT/Pt/Ti/SiO_2-interaction using AES and SIMS

anneal of Pt/Ti electrode: 700°C, 5min

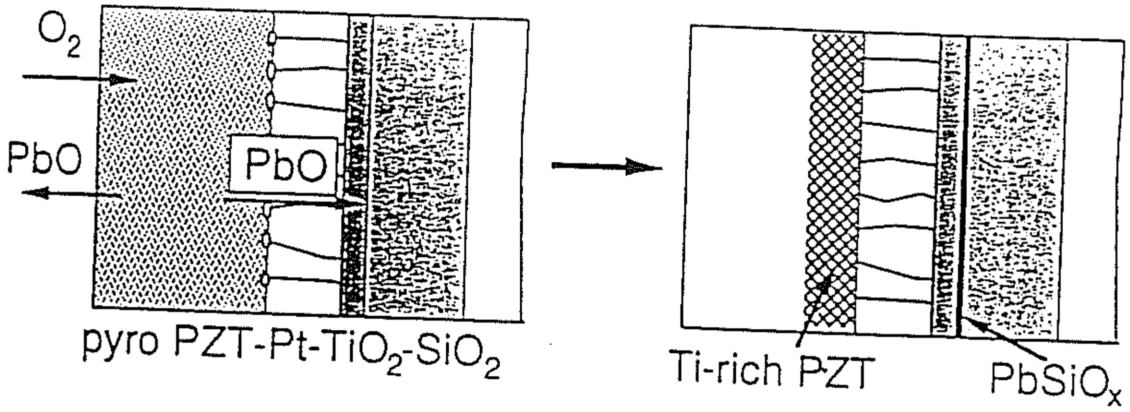


Ti/SiO_2-interface: $Ti + SiO_2 \rightarrow TiO_x + Ti_ySi_z + SiO_2 + Si + (O)$

$+ O_2 \rightarrow TiO_2 + SiO_2$

Fig.1. Material interactions after bottom-electrode annealing

PZT crystallization on annealed Pt/Ti



$PZT + TiO_2 \rightarrow$ Ti enriched PZT

$PbO + SiO_2 \rightarrow PbSiO_x$

good quality perovskite PZT is formed

Fig.2 : Material interactions after PZT crystallization

Task 2. Investigation of Ru as electrode material

We investigated Ru sputtering in IMEC and later on also received Ru-sputtered samples from VITO as part of their contribution to this project.

2.1. Ru sputtered at IMEC

Initially, we could only sputter Ru layers in IMEC, by DC sputtering from a metallic Ru-target. No reactive sputtering was possible, and all sputtering was done at room temperature. We investigated different material stacks : Ru/Si, Ru/Ti/Si, Ru/SiO2/Si and Ru/Ti/SiO2/Si.

Deposition tests of sol-gel PZT followed by the required pyrolysis and crystallization heat treatments was partially successful for the Ru/(Ti/)SiO2/Si samples, but desintegration of the structure occurred for the Ru/Si sample.

The material quality was not so good (rosette structure) and rather leaky hysteresis loops were observed.

The different as-sputtered Ru samples were subjected to a thermal anneal in air (600°C, 10', hot plate). This resulted in non-uniform oxidation, by formation of isolated RuO2 "islands" (as confirmed by AES). For the Ru/Si samples, rippling/buckling of the Ru film was observed, and also non-uniform oxidation. The Ru/Ti/Si samples, however, remained flat.

2.2. Ru samples sputtered at VITO (on IMEC substrates)

Later on, we also received similar Ru/Si, Ru/Ti/Si, Ru/SiO2/Si and Ru/Ti/SiO2/Si samples from VITO. In view of the problem of non-uniform oxidation, we performed thermal treatments of the different films in inert ambient (N/Ar) in a lamp-furnace (700°C, 5'). For all the samples, we found a partial oxydation to RuO2 at the film surface. This maybe due to oxygen remaining in the furnace during the thermal treatment. The samples without Ti (i.e. Ru/Si and Ru/SiO2) showed "holes" in the film after the anneal, the Ru/Ti/Si showed RuO2 "isolated islands, and the Ru/Ti/SiO2/Si sample showed smooth surface. Further experiments will be performed to investigate the PZT deposition on these films.

Laser Deposition of PZT Thin Films and In-situ Diagnostics of the Process

Francesco Fuso, Alfredo Iembo, Gabriele Lorenzi and Ennio Arimondo
Dipartimento di Fisica and Unità INFM, Università di Pisa,
P.zza Torricelli 2, I-56126 Pisa (Italy)
tel. +39 50 911 244, fax +39 50 48277, e-mail: fuso@ipifidpt.difi.unipi.it

Maria Allegrini
Dipartimento di Fisica della Materia, Geofisica, Fisica dell'Ambiente,
Università di Messina, Salita Sperone 31, I-98166 S. Agata (Italy)
and Unità INFM, Università di Pisa,P.zza Torricelli 2, I-56126 Pisa (Italy)
tel. +39 50 911 285, fax +39 50 48277, e-mail: allegrin@ipifidpt.difi.unipi.it

Pulsed laser ablation deposition (PLAD) has become a technique commonly used to produce thin films of different materials in the laboratory scale. PLAD offers several attractive features, such as a simple experimental set-up, the preservation of the stoichiometry between target and substrate and little substrate damage. The technique is especially suitable for refractory materials, which are difficult to be vaporized by means of other techniques and for the deposition of films with complex lattice structures. In both cases, the efficient energy coupling between the laser pulse and the plume of the ablated material is a key point for the attainment of good quality depositions.

We have applied PLAD to different ceramic materials; among them, we have deposited ferroelectric $PbTi_{0.48}Zr_{0.52}O_3$ (PZT) thin films starting from stoichiometric pellets and using either low resistivity p-doped Si [1] or $Si/SiO_2/Ti/Pt$ [2] substrates. Our set-up is based on a XeCl excimer laser ($\lambda = 308$ nm, $\tau = 16$ ns, $E = 120$ mJ), focused on the surface of the target to an energy density of 3–3.3 J/cm^2, and a deposition chamber, which can be evacuated to high vacuum ($p < 10^{-6}$ mbar) or filled with a controlled pressure of molecular oxygen gas ($p = 0.2$ mbar). The substrate is placed at a distance of 18–20 mm from the target and during the deposition is electrically heated to 560 ^oC. After the deposition, which is typically carried out with 9000 laser shots, the film is heated in-situ at 100 ^oC/min to 700 ^oC for 5 min in 1 bar of oxygen.

The as deposited films show dielectric hysteresis with typical remnant polarization and coercive fields of 0.2 $\mu C/cm^2$ and 124 kV/cm, respectively. AFM analysis of the films [2] shows a typical grain diameter of 80 nm. The surface homogeneity is fairly good (typical roughness ≈ 2–5 nm), confirming that PLA is capable of producing very smooth polycrystalline film compared with other chemical methods. However, several spherical defects, or droplets, appear on the surface. Maximum diameter and height of the droplets are in the hundreds of nm-scale, while their density is approximately 400/mm^2. The presence of such defects, which can be ascribed mainly to the non-homogeneous density distribution of the laser intensity on the target, is one of the major drawback of the PLAD method. In our experimental set-up we are improving the optical quality of the laser beam in order to reduce the droplets density.

The homogeneity of the film has also been tested through vibrational spectroscopy measurements [3]. IR and Raman spectra have been collected from different regions of the surface, with a spatial resolution of 0.02x0.02 mm^2. Raman spectra show the presence of several bands ascribed in the literature to the PZT material. The comparison with a spectrum taken from the target shows negligible differences in the position of the bands, indicating that the stoichiometry of the film is similar to that of the target. The homogeneity of the film results fairly good over all the film surface (7–8 mm). Furthermore, an original non-obtrusive method has been developed in order to measure the film thickness. By analysing the oscillations in the Raman and IR scattered light as a function of the collection point and measuring the optical constants of the film, it is possible to derive the thickness with a very good accuracy. The results show that our films have a typical thickness ranging from 500 nm (at the center) to 350 nm (at a distance of 3.5 mm from the center). The corresponding deposition rate is 0.4–0.5 Å/shot.

Furthermore, we have developed two in-situ diagnostic tools in order to characterize the PLA process, based on the analysis of the fluorescence emission from the plume of the ablated material and on the collection of the charged particles in the plume, respectively. The information provided by those diagnostics are relevant for the investigation of the plume behavior (dynamics and change of composition) during its expansion from the target toward the substrate. For PZT we have found [4] that a relatively dense and hot plasma is created after laser-target and laser-plume interaction ($n_e = 7 \times 10^{17}$ cm^{-3} and $T_e = 14000$ K at a distance d = 1 mm from the target). During the expansion of the ionized plume, due to the collisional interactions with the environmental oxygen molecules and to the cooling experienced by the plume, several reactive mechanisms can take place, giving rise to the formation of oxide molecules [1] and clusters [5]. The arrival onto the substrate of species with different states of aggregation can explain several PLA peculiarities (growth of complex structures and preservation of the stoichiometry). Furthermore, the comparison of the diagnostics results with the prediction of a theoretical model, at the moment under development [6], sheds light on the role of the main process parameters (d, I p_{gas}) and helps in adjusting the parameters in multi-target/multi-layer PLAD.

Indeed, PLAD can be used for virtually any kind of materials and the proces parameters can be easily controlled, so that PLAD represents a very promisin technique for the production of multi-layer structures. We have recently built a ne deposition chamber equipped with a multi-target holder, which permits sequential in situ depositions of up to four layers of different materials. Our aim is to produce b PLAD a multi-layer structure enclosing the PZT ferroelectric film between bottom an top electrodes. Among the various materials suitable to be used as electrodes, besid the superconductive YBCO, already deposited in our laboratory [7], we ar investigating the feasibility of RuO_2 films by PLA. Preliminary results show tha conductive RuO_2 thin films can be deposited on silicon based substrates starting fro a pressed RuO_2 powder target. The in-situ diagnostics have shown that Ru^+ an RuO_2^+ ions are present in the plume obtained from ablation of the target at $I_L = 2.$ J/cm^2 and $p_{gas} = 0.1$ mbar. The film produced on a Si/SiO_2 substrate, heated at $T_{sub} =$ 500 °C and placed at a distance d = 28 mm from the target, shows, as deposited, resistance of 0.37 Ω for an estimated thickness of few thousands of angstroms. Th temperature dependent resistance exhibits a metallic behavior in the range 300–100 K.

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COST 514

MATERIALS FOR A FERROELECTRIC CAPACITOR STACK WITH DIRECT CONTACT TO SILICON.

IMEC-MTI-VITO-Univ. of Pisa

Contribution of VITO

1. Introduction

Ferroelectric thin films such as lead zirconate titanate (PZT) are widely investigated for their applications in nonvolatile random access memories. Recent studies have shown that ruthenium (Ru) and ruthenium oxide (RuO_2) and other metaloxide electrodes give capacitors with better fatigue properties compared to the normal Ti/Pt electrodes.

2. Aim of the work

This report gives an overview of the activities at VITO during the first year of the COST 514 action on Ferroelectric Ceramic Thin Films. Since VITO is receiving no funding for this work, our research activities were limited to the deposition of Ru and RuO_2 thin films. These films will be used by other partners in the project to make FECAP's.
The aim of this work is to deposit Ru and RuO_2 thin films on Si (111) and SiO_2 substrates, by means of the r.f. diode sputtering technique. During the first year, we investigated the influence of oxygen partial pressure in the gas mixture, the substrate material and heat treatment after film deposition, on the chemical composition and crystalline structure of RuO_x thin films.

3. Experimental details

A r.f. diode sputtering system was used for Ru and RuO_2 thin film deposition. The sputtering target used was a 2-inch disk of Ru-metal. The substrates were (111) Si and Corning 7059 glass. Typical sputtering conditions are listed in table 1. All experiments were carried out at room temperature.

Target	Ru
Substrate	Si (111) Corning 7059 glass
Sputtering gas	Ar/O_2-mixture
Total gas flow	15 sccm
Total gas pressure	1 Pa
RF-input power	200 W

Table 1. Sputtering conditions

Crystallography was performed by X-ray diffraction (XRD). Chemical composition analysed with Electron Probe Micro Analysis (EPMA). Film thickness was measured by height measurement using a Dektak profilometer
Some RuO_2-samples were heat treated in air at 500°C for 30 minutes .

4. Results and discussion

4.1 Chemical composition

All films obtained with O_2 in the sputtering gas were found to have a Ru/O-ratio of 1/2. points to the compound RuO_2.

4.2 Crystalline structure

4.2.1 Influence of oxygen partial pressure p_{O_2}

Figure 1 shows XRD-patterns of Ru and RuO_2 layers deposited on Si (111) under vari oxygen partial pressures. Film thickness varies over the different samples, so interpretatio peak intensities is not recommended, also due to the overlap with strong peaks of the Si(1 substrate. Pure Ru metal appeared when no oxygen was added to the argon gas. With C Pa oxygen partial pressure, RuO_2 occured by means of the (110) and (211) lines. Fur increasing the oxygen partial pressure to 0,50 Pa leads to a (101) preferred orientation of RuO_2 layer. The lattice parameter (a) of the typical tetragonal structure is slightly increa compared to single crystalline RuO_2, indicative of a small grain size and high inter stresses

4.2.2 Influence of the substrate material

The influence of the substrate material (Si(111) and glass) was investigated at two differ oxygen partial pressures: 0,07 and 0,13 Pa (figures 2 and 3). The results on glass confirm previous measurements on Si(111). Again with increasing oxygen partial pressure, preferred orientation changes from (110) to (101)
No clear influence of substrate material on layer orientation was observed.

4.2.3 Influence of heat treatment

Figure 4 shows a detail of the XRD-pattern of a RuO_2 layer on Si(111) (p_{O_2} = 0,13 F before and after heat treatment at 500°C during 30 minutes in air.
The (101) peak intensifies and shifts to higher 2θ-values, comparable to single crystalli RuO_2. This results in a decreased lattice parameter (a), probably due to stress relaxatio Increasing peak intensity points to increasing grain size and crystallinit

5. Conclusion

R.f. diode sputtering yields stoichiometric RuO_2 thin films in a large range of oxygen partial pressures. Increasing oxygen partial pressure changes film orientation from (110) to (101). No clear influence of substrate material was observed. Heat treatment after deposition normalises lattice parameters.

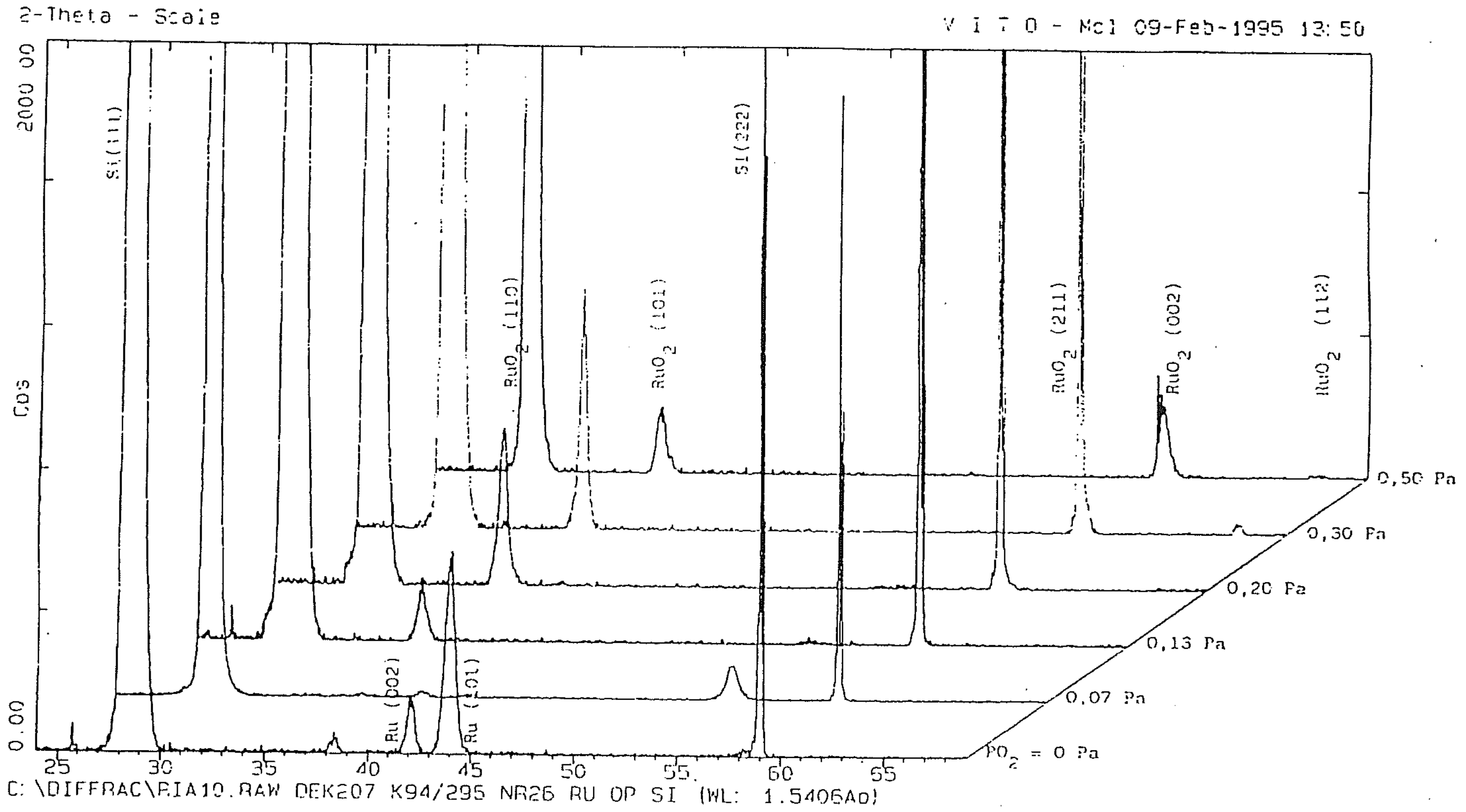


Fig. 1 : XRD patterns of Ru and RuO$_2$ thin films deposited on Si(111)

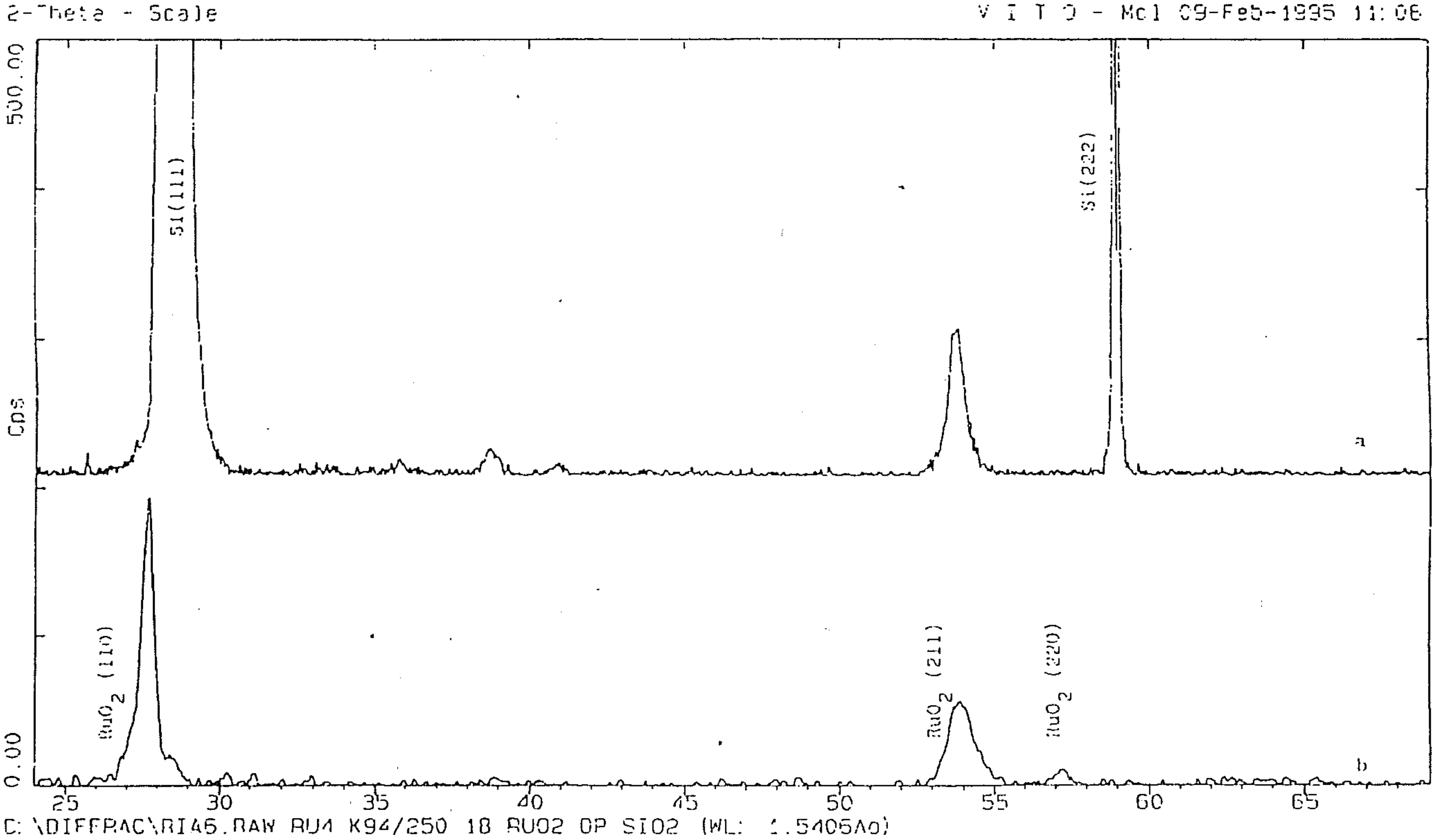


Fig. 2 : XRD patterns for RuO_2 thin films on a) Si(111) and b) glass with PO_2 = 0,07 Pa

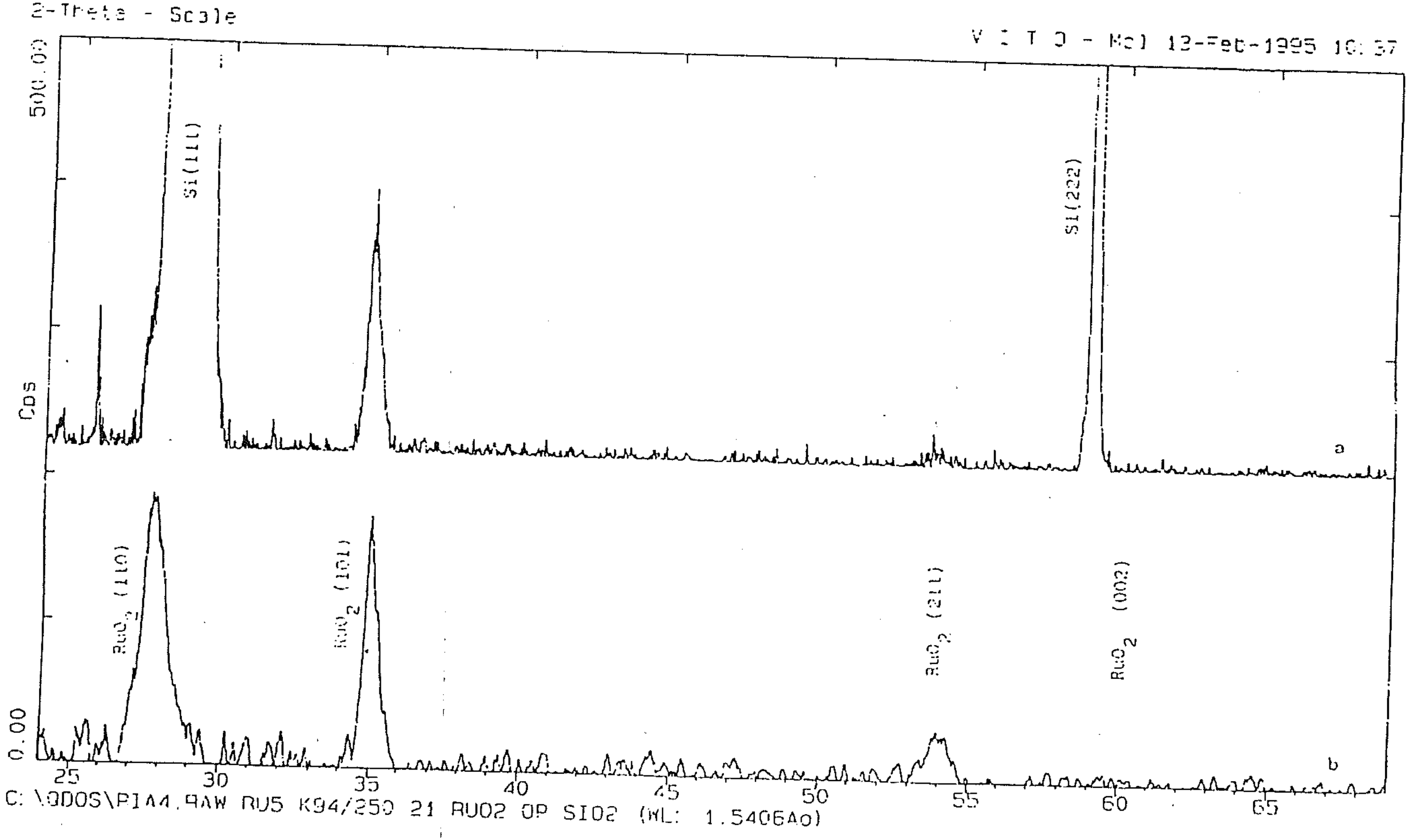


Fig. 3 : XRD patterns for RuO thin

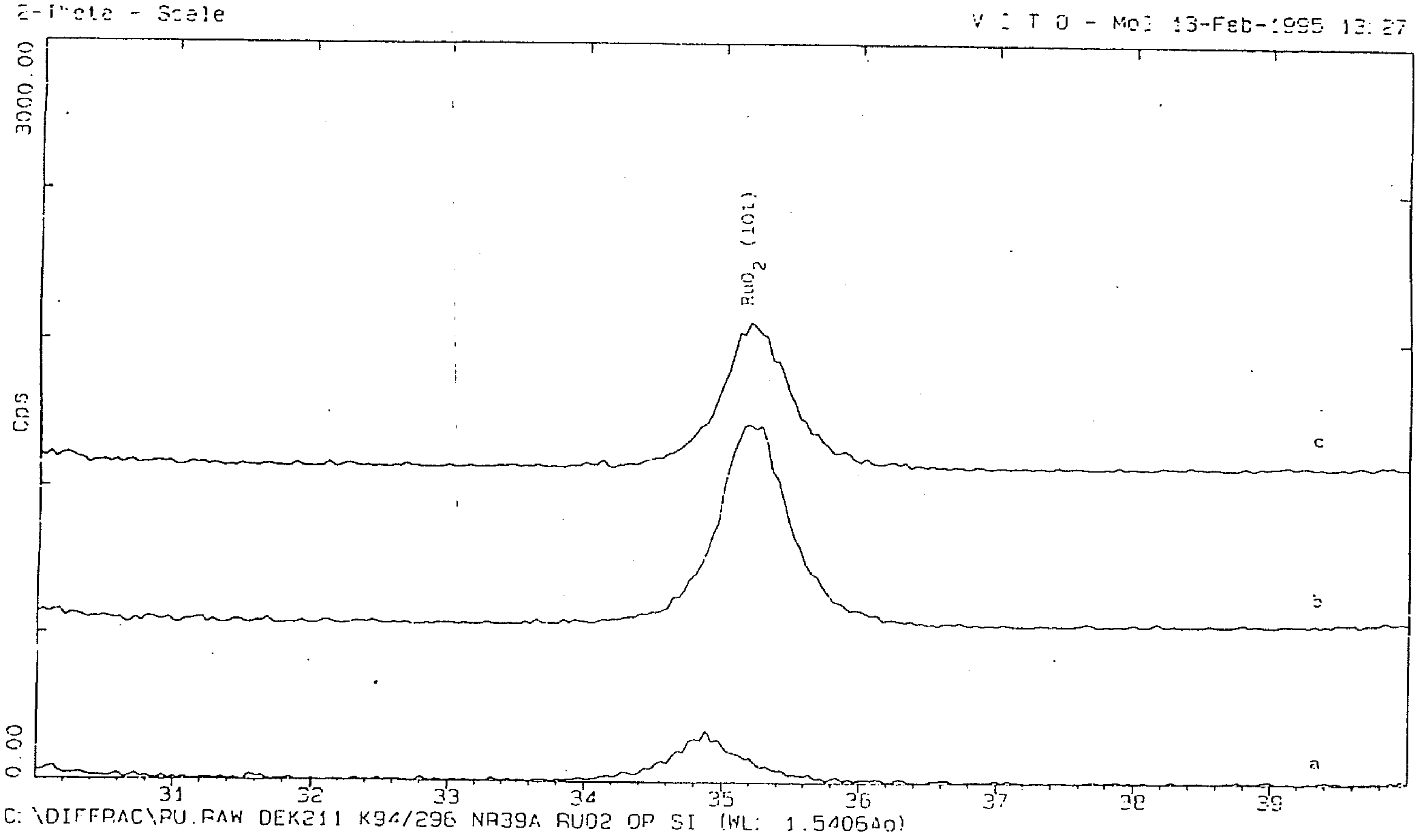


Fig. 4 : XRD patterns for RuO_2 thin film (PO_2 = 0,13 Pa)
a) before and b) and c) after heat treatment
at 500°C during 30 minutes in air

Report on COST 514 Action FERROELECTRIC CERAMIC THIN FILMS

Project: MATERIALS FOR A FERROELECTRIC CAPACITOR STACK WITH DIRECT CONTACT TO SILICON

Group: Centro Interdipartimentale Materiali e Tecnologie dell'Informazione (MTI), Università di Parma. V.le delle Scienze, I-43100 PARMA, ITALY.

B.E. Watts Istituto MASPEC/CNR, Via Chiavari 18a, I-43100 PARMA, ITALY.
Tel: +39 521 269207 Fax: +39 521 269206
email leccabue@prmasp.pr.cnr.it

1. Development of apparatus to measure fatigue

The objectives were to construct an apparatus capable of studying the fatigue characteristics of ferroelectrics for use in non-volatile memories. Ideally the number of read/write cycles which a capacitor should support is 10^{15} but 10^{12} is acceptable. To test this within reasonable experimental times (10 days) frequencies of 1 MHz are needed. The original apparatus constructed at the Univ. of Parma worked at a frequency of 10 KHz the new apparatus works with variable frequencies up to 2.5 MHz. In addition, to improve the statistics of the experiment the apparatus is able to fatigue and measure 16 capacitors in parallel.
The scheme and design of the apparatus is shown in the figures.

Figure 1 A personal computer controls the measurements and holds the boards which generate the wave form for the fatigue and pulsed hysteresis (AWFG), data acquisition (DAS16) and control of the relays (PIO12). The apparatus itself consists of eight printed circuit boards each running on two capacitors. Considerable difficulties were encountered in a first version of the apparatus with parasitic capacitances. Because of this the whole board had to be redesigned and constructed.

Figure 2 The set up of the measurement boards themselves is shown. Each capacitor is connected to its own Sawyer and Tower circuit with a reset switch in order to short the linear capacitor and an operational amplifier which decouples the sample from the common line so that the other samples can be measured when it short circuits. The relays which switch from measurement to fatigue are shown.

Figure 3 The apparatus has been tested on samples prepared by sol-gel and has been found to be completely functional. Some measurements are shown by the wave form from the Sawyer and Tower circuit. Note the wave form before fatigue (solid line): asymmetric about the zero line because one starts with a polarised capacitor. The wave form after fatigue (dotted line) drifts, probably because of leakage currents in the ferroelectric, and had to be reset by shorting the linear capacitor after hysteresis 3 cycles. The pulsed hysteresis measurements are shown a slow polarisation rate of these samples.

Currently a series of $Pb(ZrTi)O_3$ samples with different Zr:Ti ratios are under test. Future work use the apparatus to study the effects of frequency on fatigue rate. To do this smaller ferroelectric capacitances are needed to avoid problems with the slew rate and durability of the "op amps". This series of samples is showing rather different fatigue behaviour to previous batches; the drift mentioned above was observed which may be related to the preparation of the PZT or the thermal oxidation of the substrate.

2. Study of films produced by sol-gel

In addition to the electrical characterisation PZT films have been characterised structurally and morphologically. This has been carried out in collaboration with the "Dipartimento di Scienze dei Materiali e della Terra. Università degli Studi di Ancona". Grazing angle X ray diffraction and transmission electron microscopy (TEM) have revealed details of the substrate and PZT as a function of depth.

X ray diffraction on the substrate showed that after thermal oxidation of the titanium revealed titanium oxide or suboxides (TiO_2. Ti_5O_9. Ti_5O_{11}, Ti_4O_7 etc.). The PZT films were almost completely perovskite with only a small peak corresponding to the pyrochlore phase ($Pb_2Ti_2O_6$). Zirconium rich films ($PbZr_{0.75}Ti_{0.25}O_3$) formed the perovskite phase readily, with only a slight presence of pyrochlore near the surface. The titanium rich films ($PbZr_{0.25}Ti_{0.75}O_3$) contained traces of Ti oxides.

Electron microscopy showed that the substrates were rather rough. The PZT films showed different morphologies when seen by TEM. Zr rich films had rosettes often reported in the literature; samples for TEM were difficult to prepare because film. probably under mechanical stress peeled away from the substrate during thinning. Ti rich material had no such problems and in fact well defined columnar grains, as seen in cross section. and within the grains well defined ferroelectric domains could be seen. The domain walls were inclined at approximately 45° to the growth direction.

3. Completion of pulsed laser deposition apparatus

The laser deposition apparatus has been completed and the first films are currently being deposited. The completion involved the following items.

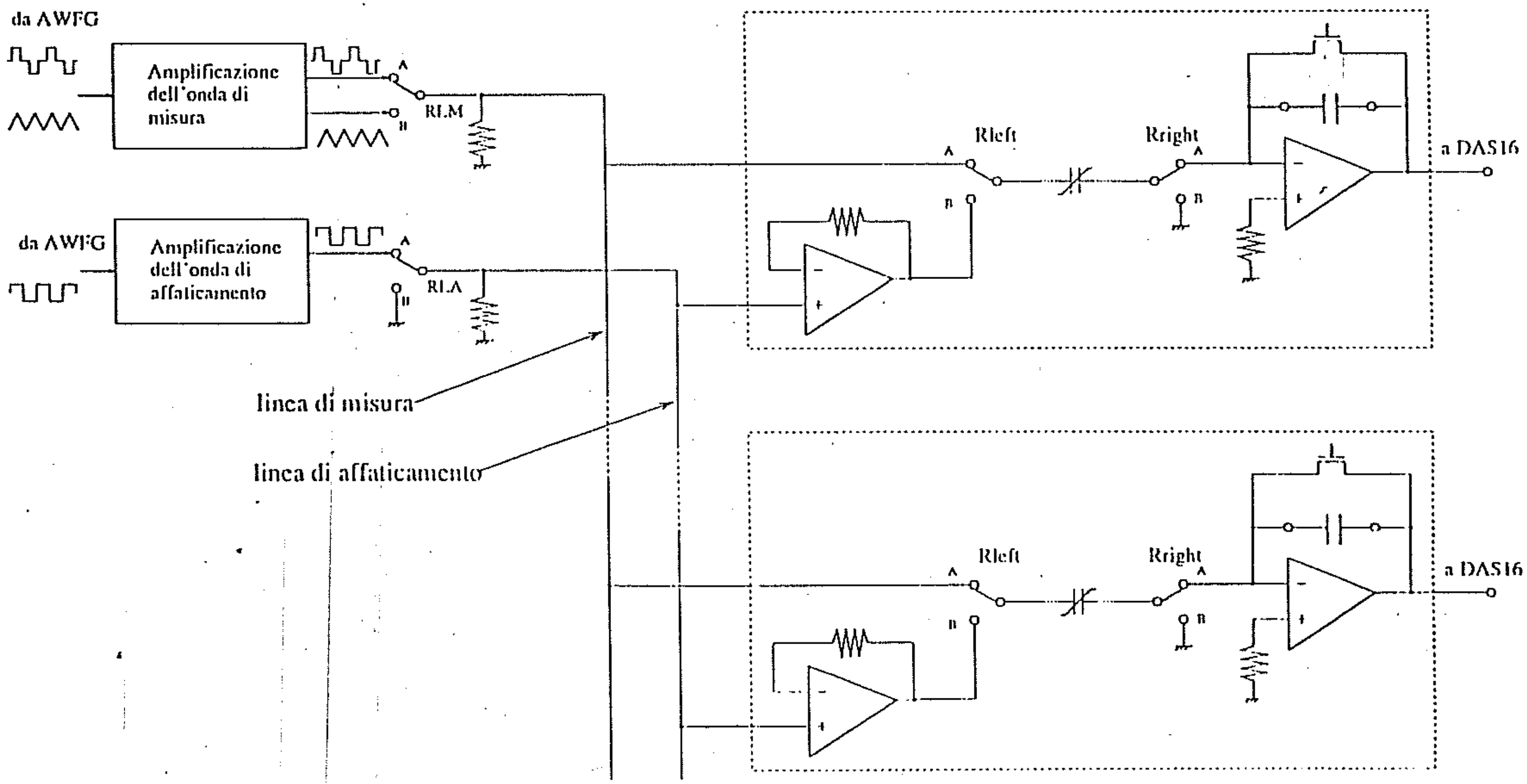
(i) Testing of the vacuum chamber. The performance of the vacuum system is more than adequate for the epitaxial deposition of oxides (10^{-7} Torr). The substrate heater is built in house and, although it shows good stability the heater element has a short lifetime.

(ii) Commissioning of the laser. The required safety feature were installed and inspected before the laser could be used (operator protection. gas handling). The problems which were anticipated with beam divergence have not been seen, however, if this does appear the pulse energy (> 400mJ) should be sufficient to allow us to trim the edges of the beam and focus tightly onto the target.

4. Projects and collaborations

Since the last Action meeting in Aachen the group has been assigned 30.000.000 lire for a national project in collaboration with the Dipartimento di Fisica. Università di Pisa. IROE/CNR. Firenze and Dipartimento di Scienze dei Materiali e della Terra, Università degli Studi di Ancona. In addition, 10 month studentship (EC funding) will be given to a graduate student from the group in Pisa to work on the laser deposition in Parma.

IMPOSTAZIONE DEL SISTEMA DI MISURA



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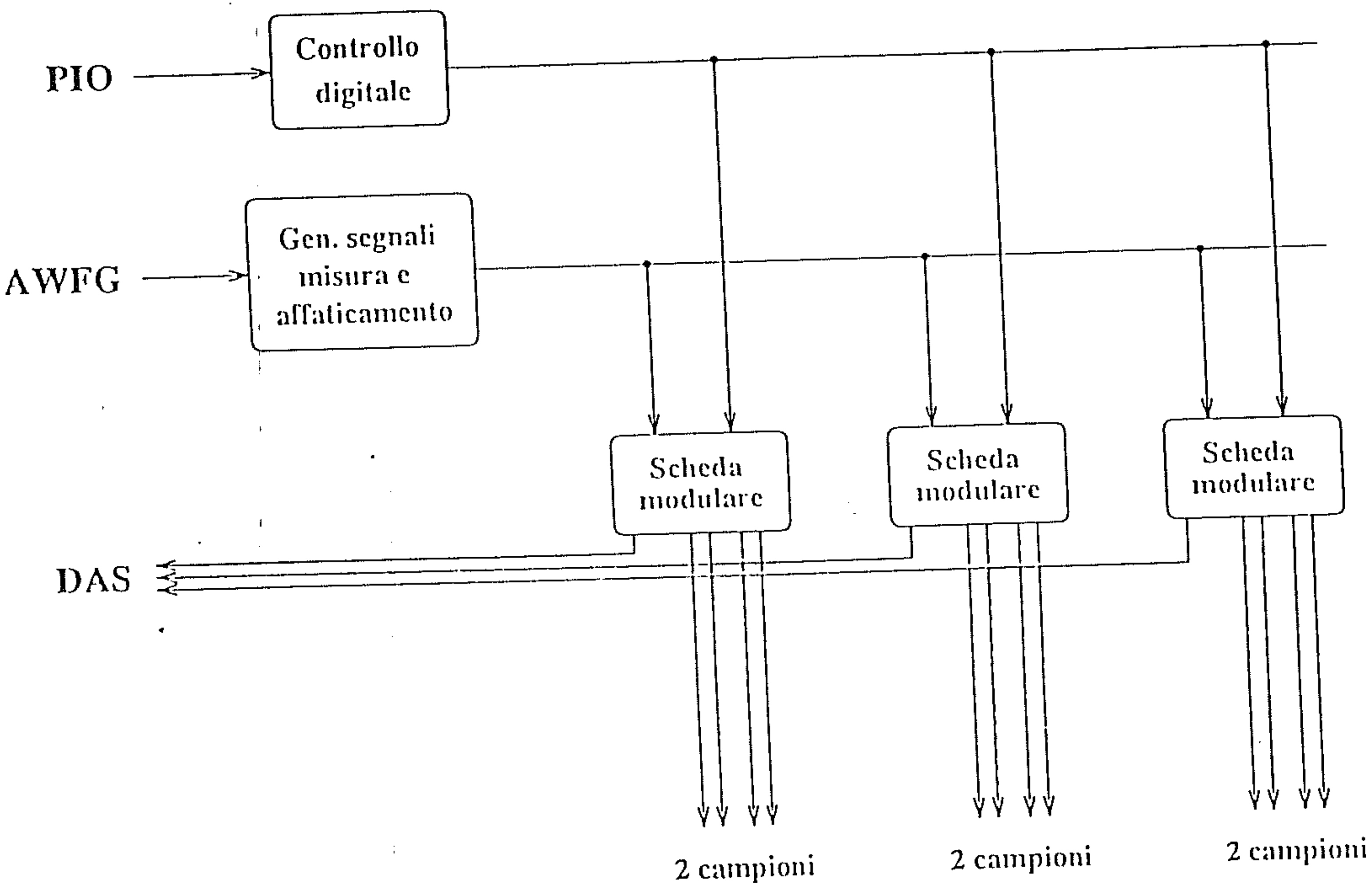

PIO

AWFG

DAS

Controllo digitale

Gen. segnali misura e affaticamento

Scheda modulare

Scheda modulare

Scheda modulare

2 campioni

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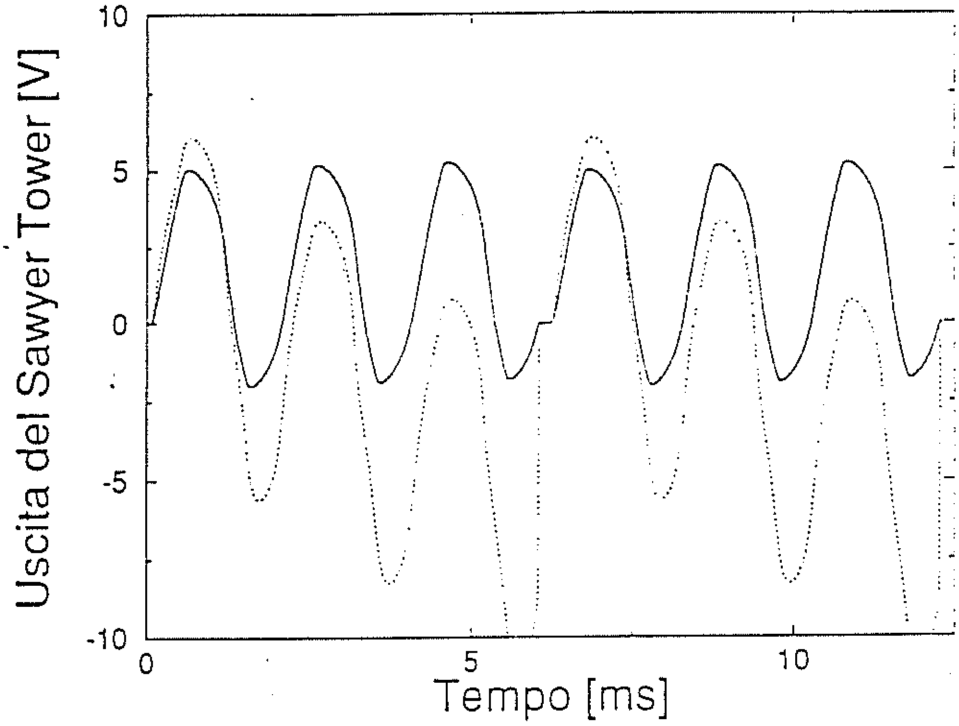
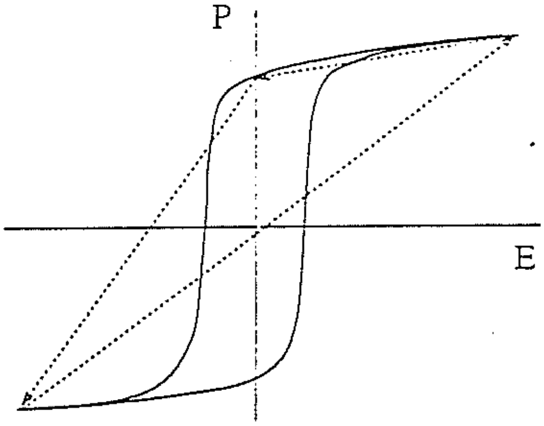
FORME D'ONDA

- Onda d'ingresso triangolare





Dopo l'affaticamento del campione:

- Aumento della polarizzazione commutata
- Aumento della corrente di leakage

NSTITUT DE PHYSIQUE APPLIQUÉE

ÉPARTEMENT DE PHYSIQUE

HB-Ecublens CH-1015 LAUSANNE Suisse
éléphone: +41 (0)21 - 693 11 11
éléfax: +41 (0)21 - 693 46 66 Télex: 454 478

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

COST 514 : FERROELECTRIC CERAMIC THIN FILMS

roject: Novel polarised ferroelectric thin films for silicon integrated devices

pplicant: Prof. Francis Lévy
Institut de Physique Appliquée
Ecole Polytechnique Fédérale de Lausanne
CH-1015 LAUSANNE (Switzerland)

esponsible scientist: Dr. P.H. Schmid, IPA-EPFL

oworkers: C.H. Kohli
X.X. Qu

PROGRESS REPORT FOR THE PERIOD 01.05.1994 - 31.01.1995

Summary of the work realized

1. *Sample preparation*

The pyroelectric compound $LiTaO_3$ is chosen as a first priority for the two following reasons:

- $LiTaO_3$ has a high Curie temperature of 665°C
- $LiTaO_3$ has a high pyroelectric coefficient of 176 $\mu Cm^{-2}K^{-1}$ (at room temperature).

Thin films are deposited on various substrates by reactive magnetron sputtering from ceramic or pressed powder targets. The deposition parameters are:

- reactive plasma : 0.1 Pa (40% O_2, 60% Ar)
- substrate temperature: 20 - 110°C (no heating)

The deposited films are amorphous, with a thickness of 250-300 nm.

Considering the final goal of integration in silicon technology, various substrates are used including contact materials:

- SiO_2, Si, oxydized Si
- RuO_2/Si, Pt/Si, Pt/Ti/Cr/Si, $Pt/SiO_2/Si$

Beside obtaining the correct pyroelectric phase with the highest pyroelectric coefficient, the solid state reactions and diffusions at interfaces constitute the most critical problem to be investigated.

The deposited films are crystallised after a normal thermal treatment in air or in pure oxygen during 1 h. A rapid thermal annealing (RTA) during 45 s also leads to the expected crystallised phase. The process temperature varies between 400 and 650°C, the most suitable one appearing to be around 600°C.

1.2 *Film characterisation*

Structural characterisations are carried out by X-ray diffraction (XRD) measurements in various geometries, by scanning electron microscopy (SEM), and in specific cases by transmission electron microscopy (TEM), in particular in cross-sectional samples. Polycrystalline films are obtained after a thermal treatment at 500°C. They are partially textured and the grain size increases from 20 to 40 nm with increasing annealing temperature.

Chemical characterisations by secondary ion mass spectrometry (SIMS) and depth profiling allow to determine the composition of the films. The Li/Ta ratio corresponds to the stoichiometric ratio. However, no reliable quantitative value of the oxygen content can be obtained.

1.3 *Novel ferroelectric films*

A prospective investigation deals with the pyroelectric material $SbNbO_4$ with a Curie temperature $T_c = 410°C$ and a pyroelectric coefficient p 300 $\mu Cm^{-2}K^{-1}$. The first step is to synthesize the compound and to press the target. Thin films are deposited by sputtering and the composition of the work plasma significantly influences the phases present in the deposited films. Preliminary structural and chemical characterisations indicate that thin films of the suitable composition and properties can be expected.

1.4 *Measurement equipment*

The necessary equipment is acquired and built. In particular, it is expected to measure the permittivity on a broad range of temperatures, as well as the pyroelectric coefficient with a differential technique at a highly stabilized temperature.

2. Summary of the results

The most important results of the first period of the project are:

- $LiTaO_3$ can be obtained in the form of crystallized thin films and with the correct composition;
- various reactions at the interfaces hint that rapid thermal processes and/or barrier layers are necessary;
- the novel, less known pyroelectric compound $SbNbO_4$ can be obtained in the form of thin films.

3. Collaborations

Stimulating exchanges (samples, experience, results) with

- Dr. D. Wouters	IMEC, Leuven/Belgium
- Dr. B. Watts	MASPEC-CNR, Parma/Italy
- Prof. N. Setter	LC-DMX-EPFL, Lausanne/Switzerland

4. Financial report

Contribution delayed.

FL/cz

09.02.1995

PREPARATION AND CHARACTERIZATION OF FERROELECTRIC THIN FILMS BY SOL-GEL PROCESSING USING UREA

Macit ÖZENBAŞ
Dept. of Metallurgical Engineering
Middle East Technical University
06531 - Ankara / TURKEY

Objective

Ferroelectric Ceramic Thin Films are non-metallic solid thin films that possess spontaneous polarization which can be reversed by an external electric field. Due to these unique properties. ferroelectric materials are used in various applications such as capacitors. piezoelectric materials (transducers), pyroelectric detectors, electro-optic materials, thermistors and dielectrics. The objective of the project is to promote a research for the preparation of ferroelectric thin films using homogeneous precipitation from aqueous solutions in the presence of urea [$(NH_2)_2CO$]. The details of the technique are given in the background section. The coating of the films was accomplished by dipping the substrates into the suspension of the powders. The films produced were characterized by using XRD and SEM for their structures and by piezometer and resistivity techniques for their properties. The investigation of the films and film/substrate interfaces by SEM and TEM can provide useful data.for the interpretation of ferroelectric properties. Also. the microstructural data can supply some information about the reliability of the films. Another point of the electron microscopy work is the possibility of the investigation of growth mechanisms for these films.

Background

Preparation and synthesis conditions of uniform (preferably. monosized and monodispersed) and chemically homogeneous particles of ferroelectric ceramics (PZT. PLZT, $BaTiO_3$, $PbTiO_3$, $Sr_2Nb_2O_7$. $Ca_2Nb_2O_7$, $Sr_{0.5}Ba_{0.5}Nb_2O_6$, etc.) have been investigated, in the recent years. by numerous researchers [1-3] by using sol-gel/alkoxides. hydrothermal synthesis, and co-precipitation techniques.

The widely used precursors (in sol-gel techniques) for the preparation of PZT thin films include metal alkoxides such as lead acetate trihydrate, titanium isopropoxide and zirconium isopropoxide or zirconium isobutoxide. Since these alkoxides are extremely sensitive to moisture present in the ambient, their processing require a strictly controlled atmosphere which could be obtained by using a glove box. Multiple distillations (regular and vacuum) would also be necessary to remove the esters formed from the lead and PZT precursor solutions.

Preparation of PZT ceramic powders from the organic sols of citrates by the Pechini [4] method has recently been studied [5]. Because of the formation of a polyester resin during the synthesis that needs further heating (up to 800°C) to burn off the organic residue. XRD should not be the only available tool to check on the phase purity of the calcined product. Analytical tools like fourier-transformed IR spectroscopy and TGA should be accessible to verify the proper removal of carbonaceous residues when working with the Pechini method.

The oxalate method exemplified in the synthesis of lead barium titanate powders [6] is shown to produce high-purity, fine-grained but agglomerated, single-phase titanates by reacting barium- and lead-titanates with ammonium titanyl oxalate at low pH and low cation concentrations. It should be noted that the precursors and intermediates formed (oxalates) in this technique still requires a very strict control (such as IR spectroscopy) over the conversion-to-oxide step.

The coprecipitation method basically involves the titration of aqueous solutions of Pb, Ba, etc. salts (nitrates) and $TiCl_4$ in stoichiometric (or desired) quantities, in the presence of a hydrogen peroxide solution, against ammonia at a low temperature (such as 65°C) [7]. On the other hand, the precursors prepared with the nitrate-EDTA route produced fine but quite agglomerated particles of PZT composition [8]. In this route, $ZrCl_4$, and $Pb(NO_3)_2$ salt solutions were added gradually to the EDTA solution at a pH of 5, followed by 1 h of equilibriation at room temperature. The formed gel was then heated in a vacuum oven at 80°C for about 24 hours to produce the precursors.

The above were about all the methods tested previously in the synthesis of ferroelectric ceramic powders. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely the homogeneous precipitation from aqueous solutions. This method involves reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 75-98°C to produce the precursors in about one hour. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia. Akınç, et al. [9] prepared spherical, monosized yttrium oxide precursor particles using urea and yttrium salt (nitrate or chloride) and $Y_3Al_5O_{12}$ using urea, yttrium- and aluminium nitrates. They were also successful in preparing uniform and chemically homogenous powders of $GdAlO_3$, $LaAlO_3$, and $GdAl_{11}O_8$. Therefore, this technique works in some systems quite well when one has the appropriate salts of the cation of the desired composition.

Preparation of $Pb(Zr,Ti)O_3$ Films

The required materials for homogeneous precipitation are basically $ZrCl_4$, $TiCl_4$ and $PbCl_2$, together with some urea. The stock solutions of lead, zirconium and titanium were prepared using the chlorides of these constituents. The concentrations studied are given below

Pb^{+2}	0.01 - 0.075 M
Zr^{+4}	0.1 - 0.5 M
Urea	0.1 - 0.5 M

The process involved the addition of stock solutions in proper amounts to form the desired compound at the end, and urea to sufficient water in order to obtain a clear solution. Ammonium hydroxide was used to regulate the pH of the solution. The resulting PZT solutions were gelled by holding at 90°C for 1 to 2 hours while magnetically stirring. The starting pH of the solutions was between 0 and 1. However, the pH gradually increased to 5 - 5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution at these pH values. The precipitate was redissolved by adjusting the solution pH to yield gels of $Pb(Zr,Ti)O_3$.

XRD patterns were obtained for the dried precipitates, and also for the powders heat treated at 300 - 800°C in open alumina crucibles in air. Particle size and morphology were observed from SEM micrographs, which showed that the particles are of sub-micron size. EDX analysis were carried out on the same samples to have information about elemental distribution.

The substrate materials for PZT slurries (prepared from the produced powders) are platinized silicon and sapphire. The coating of the films was accomplished by dipping the substrates into the suspension of the powders. The next step in producing the films will be the use of a technique similar to spin-casting (e.g., with a centrifuge working minimally at about 3000 rpm; we are now working to build up such a centrifuge; by placing the substrate within a centrifuge tube or container together with the suspension of the powders).

The microstructure and characterization studies on these films are continuing.

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INTERIM REPORT

PART 1

COST 514

FERROELECTRIC CERAMIC THIN FILMS

REPORTS DELIVERED AT
FOURTH COST 514 WORKSHOP IN MADRID, MARCH 1996

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Contents

Preface

The Management Committee of COST 514 decided to summarize the activity of first 3 years at the Workshop held in Madrid on 4-5 March 1996. Besides presentation of progress reports, the participants were asked to deliver written Annual Report 1995. The progress reports together with invited lectures were published by CSIC Madrid in April 1996. The booklet contains 44 pages information on present status of COST 514 projects.

We believe that the achievements of first half of the COST 514 Action are well documented by the abstracts from the Workshop and present reports. It is encouraging to see increasing interest of industry in the field. Future activity will continue in the standard way within 5 group projects and regular spring meetings at a workshop.

M. Kedro
COST 514 Management Committee
Scientific Secretary

testing. It was shown that microstructure and consequently dielectric constant of $BaTiO_3$ films can be tailored by the structure of barium carboxilates and titanium alkoxides (RWTH).

Crystallisation, orientation and microstructure of sol-gel derived PZT films were studied in several laboratories (IMEC, Luleå, Sheffield, EPFL). In collaboration with EPFL and Luleå the crystallisation of PZT layer was studied in situ using high temperature X-ray diffraction. Detailed TEM analysis of sol-gel PZT samples confirmed the deteriorated effect of pyrochlore phase on the surface on the fatigue of films. It was also applied to characterise thick PZT films (up to 7 μm) on Pt coated ZrO_2 (EPFL, Sheffield). The mechanisms that relate the orientation and chemical composition of Pt electrode and orientation of sol-gel PZT layers with various Zr/Ti ration were proposed by IMEC. A new aspect of TiO_2 enriched Pt surface on the nucleation of perovskite phase was presented.

There were very strong activities in physical characterisation of thin films (EPFL, IMEC, RWTH).

EPFL's work concerned the degradation phenomena in electromechanical properties of PZT films. Experimental set-up has been developed on the basis of double-beam laser interferometer which allows to measure ultrasmall electric field-induced displacements in piezoelectric thin films. The interferometer technique is successfully applied for the evaluation of piezoelectric response of PZT films on thick substrates and on thin membranes. It is shown that effective piezoelectric coefficients of 100-150 pm/V and strains of $(2\text{-}3)10^{-3}$ can be achieved with the compositions near the morphotropic phase boundary. Piezoelectric fatigue has been investigated in sol-gel PZT films. It was found that bipolar fatigue results in a significant polarisation offset while unipolar fatigue induces an internal bias field. Qualitative explanation of both effects is proposed. Piezoelectric ageing has been studied in sol-gel PZT films. It was shown that ageing rate strongly depends on the poling conditions and on the internal bias field direction. A qualitative model of ageing is proposed which relates the loss of piezoelectric activity with polarisation retention.

IMEC worked on various aspects of reliability of ferroelectric capacitors based on PZT thin films.

Summary of the activities in the year 1995
COST 514 - Ferroelectric Thin Films

Group project: Reliability of Ferroelectric Thin Films

Participants:	B1:	IMEC, Division MAT - ARS, Leuven, Belgium, Dr. D. Wouterss (IMEC)
	CH1:	EPFL, Laboratoire de Céramique, Lausanne, Switzerland, Prof. N. Setter (EPFL)
	D1:	RWTH Aachen, Institut für Werkstoffe der Elektrotechnik, Aachen, Germany Dipl. Ing. G. Dietz (RWTH)
	SLO1:	"Jožef Stefan" Institute, Ljubljana, Slovenia, Dr. M. Kosec (IJS)
	S2:	Luleå University of Technology, Div. of Engineering Materials, Luleå, Sweden, Dr. T. Lindbäck and Dr. O. Babushkin (LuTH)
	UK4:	University of Sheffield, Dept. of Engineering Materials, Sheffield, England, Dr. W. Lee and Dr. I. M. Reaney (Sheffield)

The group project includes research topics related to the reliability of ferroelectric thin films, namely processing, structural and functional characterisation.

The activities and the most significant results are summarised as follows, whereas the details are described in the reports of the individual group.

Research concerned materials $Pb(Zr_xTi_{1-x})O_3$, $SrTiO_3$ and $BaTiO_3$ deposited on Pt or RuO_2 electrode on Si substrates. An attempt was made to use ZrO_2 as a substrate material as well. Concerning processing, IJS worked on sol-gel PZT and RWTH on solution processing of $BaTiO_3$. The main aspect was in the role different precursors play in the structure and properties of films. It was demonstrated for the first time that lead oxide may efficiently replace commonly used lead acetate as a precursor in sol-gel processing of PZT. Lead based PZT thin films are characterised by improved microstructure and well saturated hysteresis loop. Film was sent to EPFL for further

A measurement system was built in order to evaluate the switching and non-switching charge by applying high - frequency pulses in ferroelectric capacitors. It was found that the measured switching and non-switching charges did not depend on the width of the write (program) pulses in the range from 150 nsec to 2 msec. To investigate the sort-time retention problem, pulse measurements were applied with varying waiting times between the write and read pulses. The measured charges, however, did not reveal a dependence on this waiting time in the range from 150 nsec to 2 msec. For the FECAPs fabricated with RuO_2 electrodes, first experiments indicate that the endurance may be much improved as compared to Pt-electroded samples. Small signal measurements of the parallel capacitance C and conductance G of Pt/PZT/Pt DFECAPs were measured as function of frequency and DC bias.

RWTH concentrated its work on leakage current characterisation of $SrTiO_3$ thin films. The leakage current characteristics of $SrTiO_3$-thin films can be divided in four regimes: low-field ohmic regime, saturation regime, Schottky regime, and high-field regime. The field of dependence of the leakage current in $SrTiO_3$ thin films with metal electrodes can be described by thermoionic emission of electrodes from the cathode. But the Schottky equation needs extensions towards low fields for which an ohmic and a saturation regime is found as well as towards high fields. For high fields the deviation from the Schottky effect can be at least partially explained by a more general injection law which is valid over all temperatures and fields.

In cooperation with EPFL and RWTH transient current in PZT films prepared by sol-gel were investigated at various times. Study of thermally stimulated currents in $SrTiO_3$ films, monocrystals and ceramics was started.

Cooperation and related activities

- Prof. Setter organised the Second Workshop on Ferroelectric Thin Films at EPFL in Lausanne in February 1995.
- Short-term scientific mission: Dr. Ian M. Reaney from Sheffield visited EPFL.
- Dr. Marija Kosec visited EPFL in August 1995.
- Visit of member of EPFL to RWTH Aachen.
- Dr. Barbara Malič from IJS has been working as a post doc for a half a year with EPFL.

COST 514 : Reliability of Ferroelectric Thin Films

IMEC Activities Yearly Report

D.Wouters, February 1996

CONTROL OF THE ORIENTATION OF THE PZT AND OF THE PZT/ELECTRODE INTERFACE.

In the initial phase of the project, the laser ablation technique was used for the heteroepitaxial growth of ferroelectric capcitors. Single-crystalline MgO or $LaAlO_3$ substrates were used, on top of which LSCO ($La_{.5}Sr_{.5}CoO_3$) perovskite-electrodes were deposited by laser ablation, and subsequently also PZT by laser deposition. After deposition of LSCO top electrodes, high quality hysteresis loops were obtained, and the heteroepitaxial growth was confirmed by XRD.

It was found, however, that also sol-gel fabricated PZT, spin-deposited on LSCO/MgO resulted in the same high-quality structure. This proves that also the sol-gel deposition method can result in films of high crystal quality and hetero-epitaxial growth.

In this year, the nucleation and orientation of this sol-gel PZT on top of the standard Pt/Ti electrodes on oxidized Si substrates was studied.

It was found that PZT, except for Ti-rich compositions, is hard to nucleate on the Pt electrodes, and typically a 2-phase structure with rosette structure is obtained. However, an adequate thermal treatment of the Pt/Ti bottom electrode was found to result in good nucleation, and it was proved that this is due to diffusion of the Ti through the Pt to the electrode surface. During the thermal treatments, the TiO_x present at the surface dissolves in the PZT, resulting in locally Ti-enriched PZT which nucleates well on top of the Pt.

The nucleation of this Ti-rich PZT on Pt was found to occur in a hetero-epitaxial way. The PZT film is highly (111) preferentially oriented, corresponding to the (111) orientation of the Pt film. This heteroepitaxial growth is made possible because of the rather good lattice matching between Pt and PZT. It was furthermore established that if the Pt film contains even a minor (100) oriented fraction (which is the case e.g. for Pt films deposited on TiO_2 i.o. on Ti coated substrates), the PZT film turns to preferential (100) orientation. This can be explained by a heteroepitaxial nucleation of (100) PZT also on (100) Pt, and furthermore to a far more easy nucleation and/or growth of the (100) PZT than of the (111) PZT, resulting in a competitive growth in favor of the (100) PZT orientation.

However, for the high-Ti content PZT, we found that even on (111) oriented Pt/Ti bottom electrode, depending on its thermal pre-PZT deposition treatment, both (111) oriented and (100) oriented films could be obtained. Experiments revealed that the amount of TiO_x coverage is hereby of importance : if too much TiO_x is present at the electrode surface, it cannot be dissolved anymore into the (already high-Ti content) PZT. The PZT film is therefore not able anymore to nucleate on the (111) Pt, but nucleates instead on the TiO_2, resulting in the different orientation observed.

This ability to change the orientation of the PZT film for (111) preferential to (100) oriented films, is interesting to investigate the influence of this orientation on the FECAP properties and reliability. We indeed found a difference in hysteresis loop characteristics and in the impedance (C,G) parameters of these FECAPs, which are probably due to different ferroelectric switching mechanisms in the two materials.

FERROELECTRIC CAPACITORS WITH RuO_2 ELECTRODES

Using RuO_2 bottom electrodes obtained by reactive sputtering, we were able to successfully deposit $PZ_{.20}Ti_{.80}O_3$ by sol-gel spin-coating. Well-crystallized perovskite films were obtained as confirmed by XRD, with different orientation depending on the bottom/electrode-substrate structure.

Hysteresis loop measurements on FECAPs made by laser-ablation deposition of RuO2 electrodes, indicate very high quality hysteresis loops (very comparable to those obtained with Pt electrodes) wich show good saturation and thus no excessive leakage current.

RELIABILITY STUDY

Pulse Measurements

For the complete evaluation of the ferroelectric properties and reliability, not only the hystersis loop, but also high-frequency pulse measurements are important.

A measurement system was build in order to evaluate the switching and non-switching charge by applying high-frequency pulses in ferroelectric capacitors. We are able to apply pulses with a minimum width of 150nsec, and with pulse amplitudes up to 7V. For the fast measurements, capacitors with a top electrode area of $1000\mu m^2$ are used.

For our material, we found a good agreement between the remanent polarization P_r value from 1kHz hysteresis loop measurements and the difference between switching and non-switching charges obtained form pulse measurements with pulse widths of 150nsec, indicating a high-quality, fast switching process. In accordance, the measured switching and non-switching charges did not depend on the width of the write (program) pulses in the range from 150nsec to 2msec.

Retention analysis

It has been observed by a number of authors that part of the polarization (as measured by hysteresis loop) can relax in short times (<msec). To investigate this short-time retention problem, pulse measurements were applied width varying wait time between the write and read pulses. The measured charges, however, did not reveal a dependence on this wait time in the range from 150nsec to 2msec.

Endurance characterization

Electrical fatigue is one of the major reliability problems of the ferroelectric capacitors. Therefore, we measured fatigue by applying 2MHz bipolar pulses, and repetitively performing pulse measurements after cycling.

As expected for our samples with Pt electrodes, endurance was limited to about 10^5 cycles, after which a fast degradation of the switched charge is observed. However, using unsaturated (partial) switching at limited voltage, endurance up to 10^{11} cycles is measured, however at the expense of a reduced signal.

For the FECAPs fabricated with RuO_2 electrodes, first experiments indicate that the endurance may be much improved : using large capcitors and low frequency cycling (1kHz), no degradation of the hysteresis loop was observed after $3x10^6$ cycles. Applying the same amount of switching cycles, however, resulted already in a very strong degraded loop in case of Pt-electroded samples.

Small signal impedance measurements

Small signal measurements of the parallel capacitance C and conductance G of Pt/PZT/Pt FECAPs were measured as function of frequency and DC bias. Both components were shown to be dominantly influenced by the switching processes in the material. Therefore, comparison of different materials by measurement of only the 0V bias components may be very dangerous. It may be a better procedure to compare the impedance values at a high DC bias where the polarization is fully saturated.

DC leakage and degradation

A summary of our study of this phenomena can be found in the publication : "Electrical Conductivity in Ferroelectric Thin Films", by Dirk J.Wouters, Geert J.Willems, and H.E.Maes, presented at the EMIF-1 Conference, July 1995, Nijmegen (NL), and published in Microelectronic `Engineering 29 (1995) pp. 249-256.

Short report on the activity of EPFL/LC in COST 514 project: "Reliability of Ferroelectric Thin Films"

Degradation Phenomena in Electromechanical Properties of Ferroelectric Thin Films (A.Kholkin, EPFL)

1. New experimental set-up has been developed on the base of double-beam (Mach-Zender) interferometer which allows to separate the bending motion of substrate from piezoelectric response. The interferometer resolution (~10^{-4} Å) was significantly improved in comparison with other such systems.
2. Electromechanical properties of PZT thin films prepared by sol-gel and sputtering have been determined by interferometric technique. It was found that effective piezoelectric coefficients of 100-150 pC/N and strains of $(2\text{-}3)10^{-3}$ can be achieved with the compositions near the morphotropic phase boundary.
3. Aging of piezoelectric properties has been studied in sol-gel PZT films. It was shown that aging rate strongly depends on poling conditions and on internal bias field in the films. A qualitative model of piezoelectric aging was proposed, which relates the loss of piezoelectric activity to polarization retention.
4. Piezoelectric fatigue was investigated in sol-gel PZT films. It was found that bipolar fatigue induces a significant polarization offset and unipolar fatigue creates an internal bias field. A qualitative explanation of both effects was suggested.
5. Degradation of piezoelectric response of Si and metallic membranes coated by PZT films has been studied. The small changes of resonance frequencies and amplitudes of vibrations was explained by the change of piezoelectric coefficients of PZT films and mechanical properties of membranes with time.

Investigation of Sol-Gel PZT Crystallization Kinetics by High Temperature XRD (K.G.Brooks, EPFL/T.Lindback, O.Babushkin, Lulea Univ. of Technology, Sweden)

The crystallization kinetics of amorphous sol-gel PZT thin films were investigated using high temperature X-ray diffraction. Crystallization for different isotherms was monitored as a function of time. Phase transformation data was obtained from integrated X-ray peak intensities which were calibrated based on image analysis of the surface microstructure of the samples at the end of the isothermal treatments. An activation energy of 310 kJ/mol was obtained without assuming a specific kinetic model. From the transformation data, a TTT diagram was constructed for the ranges studied.

Investigation of DC Conduction and Thermally Stimulated Currents in Ferroelectric and Non-Ferroelectric Thin Films (A.Kholkin, A.Tagantsev, EPFL/R.Waser, G.Dietz, RWTH, Aachen, Germany)

Transient currents in PZT films prepared by sol-gel were investigated at times varying from microseconds to thousands of seconds. It was shown that Curie-von Schweidler law, which usually describes the current decay in perovskite films, is valid down to a very low measurement time. Thermally stimulated currents (TSC) were studied in $SrTiO_3$ thin films, single crystals and ceramics with different dopants. First results showed a pronounced difference in the positions and intensities of the TSC peaks. These changes are related to different microstructure and impurity levels of investigated samples

Laboratoire de Céramique
Ecole Polytechnique Fédérale - Lausanne
Switzerland

Annual progress report
(1. January 1995 to 31. December 1995)
of the project

Reliability of Ferroelectric Thin Films

Contribution

Degradation Phenomena in Electromechanical Properties of Ferroelectric Thin Films

of the
COST 514 EU Concerted Action
"Ferroelectric Thin Films"

Authors:
Dr. Andrei Kholkin
Dr. Keith Brooks
Dr Enrico Colla
Dr. Paul Muralt
Dr. Alexandre Tagantsev
David Taylor
Markus Kohli
Thomas Maeder
Prof. Nava Setter

Lausanne, February 29, 1996.

Activity

January 1995 - December 1995

Purpose of the project

1. Characterization of the electromechanical activity of PZT thin films deposted on thick substrates and on thin membranes by means of interferometric technique

2. Investigation of the degradation of electromechanical response of PZT films and film-based structures under different stressing conditions

Abstract:

Experimental set-up has been developed on the base of double-beam laser interferometer which allows to measure ultra-small electric field-induced displacements in piezoelectric thin films. The interferometer technique is succesfully applied for the evaluation of piezoelectric response of PZT films on thick substrates and on thin membranes. It is shown that effective piezoelectric coefficients of 100-150 pm/V and strains of $(2\text{-}3)10^{-3}$ can be achieved with the compositions near the morphotropic phase boundary. Piezoelectric fatigue has been investigated in sol-gel PZT films. It was found that bipolar fatigue results in a significant polarization offset and unipolar fatigue induces an internal bias field. Qualitative explanation of both effects is proposed. Piezoelectric aging has been studied in sol-gel PZT films. It was shown that aging rate strongly depends on the poling conditions and on the internal bias field direction. A qualitative model of piezoelectric aging is proposed which relates the loss of piezoelectric activity with polarization retention.

Main results:

1. Different interferometric methods were investigated for the purpose of measuring small electric field-induced displacements in piezoelectric thin films [1]. It was shown that vibrational response measured with the single-beam interferometer includes a large contribution of the bending motion of the substrate. To suppress the bending effect a high-resolution double-beam interferometer was developed. The interferometer performance was significantly improved in comparison with previously reported systems. The resolution of the interferometer was increased by more than an order of magnitude. The interferometer was shown to directly

monitor small displacements without using the lock-in technique and could be used as a strain gauge.

2. Interferometric technique was succesfully applied for the piezoelectric characterization of PZT films of various compositions prepared by sol-gel and sputtering techniques. Both piezoelectric coefficients and strains were determined as a function of the frequency and applied electric field. It was found that effective piezoelectric coefficients of 100-150 pm/V and strains of $(2\text{-}3)10^{-3}$ can be achieved with the compositions near the morphotropic phase boundary.

3. Piezoelectric aging was studied in sol-gel PZT films [2]. It was shown that aging of piezoelectric coefficients obeys the logarithmic time dependence as in bulk ferroelectric materials. The aging rate after poling at room temperature was found to depend strongly on poling conditions and to decrease considerably with the increase of poling time. Another important factor is the internal bias field in the films which accelerates the aging process when the poling field is applied against the preferred polarization direction. A qualitative model of piezoelectric aging was proposed which relates the loss of polarization activity with the polarization retention.

4. Piezoelectric degradation under bipolar and unipolar pulse conditions in sol-gel PZT films was investigated with the purpose to elucidate the nature of polarization fatigue and to evaluate the endurance of PZT films for piezoelectric applications [2-4]. No significant changes of piezoelectric coefficients were observed with stressing the film by unipolar pulses. The coercive fields for piezoelectric effect were found to shift in the direction opposite to that used for fatigue. This was considered as the built-up of the internal bias field due to the injection of charge carriers into the PZT film. On the contrary, bipolar fatigue was shown to induce a significant shift of piezoelectric hysteresis loops along d_{33} axis. This behaviour was understood as the locking of ferroelectric domains in preferable orientations. The existence of strongly polarized state in fatigued PZT capacitors was confirmed by aging experiments.

5. PZT actuated membranes were characterized with respect to the resonance frequencies, total thin film stress and piezoelectric coefficients [5-8]. The piezoelectric behaviour was analyzed by means of analytical calculations. Different experiments carried out by interferometric technique showed consistent results which seems to agree with PZT ceramics data. It was found that sputtered PZT films have an effective stress piezoelectric coefficient of about a factor of 4 larger than that of ZnO single crystal [8]. Degradation of

piezoelectric response of membranes coated with PZT films was studied under conditions imitating the work of piezoelctric ultrasonic motor [2, 6, 7]. The small changes of resonance frequencies and amplitudes of the vibrations was attributed to a change of piezoelectric coefficients and mechanical properties of the membranes with time [2].

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Participation in conferences:

1. 7th International Symposium on Integrated Ferroelectrics, Colorado Springs, USA, March, 1995.
2. 8th International Conference on Solid-State Sensors and Actuators, Stockholm, Sweden, June, 1995.
3, 1st European Meeting on Integrated Ferroelectrics, Nijmegen, The Netherlands, July, 1995.

COST 514: Reliability of Ferroelectric Thin Films

Institut für Werkstoffe der Elektrotechnik II
RWTH Aachen University of Technology

Yearly Report 1995

RECENT RESULTS ON THE LEAKAGE CURRENT CHARACTERISTICS OF $SrTiO_3$ THIN FILMS

Guido W. Dietz and Rainer Waser
Institut für Werkstoffe der Elektrotechnik II (IWE)
RWTH Aachen University of Technology
52056 Aachen, Federal Republic of Germany

The field dependence of the leakage current in $SrTiO_3$ thin films with metal electrodes can be described by thermionic emission of electrodes from the cathode. But the Schottky equation needs extensions towards low fields for which an ohmic and a saturation regime is found as well as towards high fields. For high fields the deviation from the Schottky effect can at least partially explained by a more general injection law which is valid over all temperatures and fields.

The leakage current characteristics of $SrTiO_3$–thin films can be divided in four regimes

1. **Low–field ohmic regime**

   In the low–field regime, both thermionic currents, the one flowing in direction of the applied voltage and the one flowing in opposite direction, have to be considered. The superposition of these currents yields an ohmic–like increase of the current.

2. **Saturation regime**

   The ohmic regime ends up in a saturation value which depends on the effective Richardson constant, the temperature, and the cathodic interface barrier height.

3. **Schottky regime**

   For medium–high voltages, the current–voltage characteristic is excellently described by the Schottky effect. From the slopes and ordinates of the activation energy plot and the Schottky plot, the effective Richardson constant, the barrier height, and the product of $\varepsilon_r \times w$ are obtained.

4. **High–field regime**

   At very high fields and at low temperatures the Schottky approximation fails. This can be shown by applying the general injection law, developped by Murphy and Good in 1956, to a typical $SrTiO_3$ thin film. In this regime the current density – field relation can be calculated numerically. The current is a combination of thermionic emission and field–enhanced tunneling.

5. **Depletion layer width and dielectric constant**

   The Schottky equation only contains the product of the dielectric constant "seen" by the emitted electrons and the depletion layer width. In opposition to the Schottky approximation the numerical evaluation of the complete injection law allows to calculate the width of the depletion layer unambiguously by fitting the experimental current voltage characteristic.

In our $SrTiO_3$ thin films, the depletion layer extends over the whole film thickness and the dielectric constant is $\varepsilon_r = 5.5$. This value is not the dielectric constant of the bulk nor of some interface layer. It is just the appearent e_r having an effect on the emitted electrons during the time they need to cross the barrier.

Barium Titanate Thin Films:
Influence of Precursor Chemistry and Processing on Thin Film Properties

Susanne Hoffmann, Ulrich Hasenkox and Rainer Waser
Institut für Werkstoffe der Elektrotechnik II (IWE)
RWTH Aachen University of Technology
52056 Aachen, Federal Republic of Germany

Abstract

Polycrystalline barium titanate thin films were prepared by chemical solution deposition (CSD) on platinum coated silicon substrates. The influence of precursor chemistry and processing on the morphology and electrical properties of the thin films was investigated by IR spectroscopy, X–ray diffraction analysis, scanning and transmission electron microscopy and impedance analysis.

Introduction

Dielectric thin films of $BaTiO_3$ and $(Ba,Sr)TiO_3$ are widely investigated for thin film integrated capacitors and storage capacitors in DRAM–applications. The films were deposited by sputtering, chemical vapor deposition (CVD), laser ablation, and chemical solution deposition (CSD). $BaTiO_3$ thin films, which were deposited on platinum coated silicon substrates at temperatures below 750°C are polycrystalline and exhibit a pseudocubic structure[1–10]. Epitaxial $BaTiO_3$ thin films grown by pulsed laser deposition on (001) oriented single crystals show a ferroelectric hysteresis with a remanent polarization of 4.0 $\mu C/cm^2$ and a coercive field of 12.5 kV/cm[14]. The fine grained $BaTiO_3$ thin films with permittivities between 100 and 800 show a super–paraelectric behaviour with a slightly negative temperature coefficient of the dielectric constant in the region between room temperature and 250°C[2,7,16]. No tetragonal distortion of the unit cell could be detected by X–ray analysis and therefore no phase transition from the cubic to the tetragonal phase could be observed, in contrast to what is known from bulk ceramics[11]. This fact could be attributed to the small grain size in the thin films. Uchino[12] reported, that the critical grain size of sputtered $BaTiO_3$ thin films, for which a clear separation of cubic and tetragonal phase is still possible, is in the range of 100 and 200 nm.

The permittivity of the polycrystalline thin films depends on the porosity and the grain size[11,12]. The grain size dependence of the dielectric properties of $BaTiO_3$ thin films makes it necessary to achieve an understanding of the correlation between processing, morphology, and electrical properties. In the following study of the influence of precursor chemistry and processing on the morphological and dielectric properties of $BaTiO_3$ thin films we discuss a few aspects of the above mentioned correlation.

Experimental procedure

Polycrystalline $BaTiO_3$ thin films were deposited on platinum coated silicon wafers. Different precursor solutions as well as different heating procedures were used. The structure of the films was analyzed by glancing angle X–ray diffraction on a Philips Thin Film System. The morphology of the films was studied by scanning electron microscopy on a ZEISS FE–SEM Gemini 986 and by transmission electron microscopy and HR–TEM[15].

For contacting the platinum bottom electrode a part of the film was etched by means of photolithography. At the sharp edge the film thickness was measured with a DEKTAK profilometer. Electrical measurements were performed on Pt / $BaTiO_3$ / NiCr–Au configurations using a HP4275 multi–frequency LCR bridge with a 10kHz signal.

In the following we discuss steps of the CSD–process, which are relevant for the microstructure of the thin films. These are the barium and titanium precursor chemistry, the concentration of the spin–on solution and the heating procedure.

Figure 1 shows the flow diagram of the process. As Ba–precursors we used different carboxylates, starting with the acetate and ending with the 2–ethylhexanoate.

The investigated Ti–precursors were pure titanium butylate and $Ti(OBu)_4$ stabilized with 2 mols acatylacetone.

The molarity of acetate and propionate based solutions was varied between 0.2 molar and 0.5 molar. The effect on the thin film properties was studied by SEM and impedance analysis.

In the standard heating procedure each coating was heated at 750°C and the whole film was annealed at 750°C or 800°C.

In the crystallization study each coating was pyrolyzed at 450°C and the whole film was sintered at temperatures between 550°C and 800°C. The crystal structure of the films was analysed by X–ray diffraction.

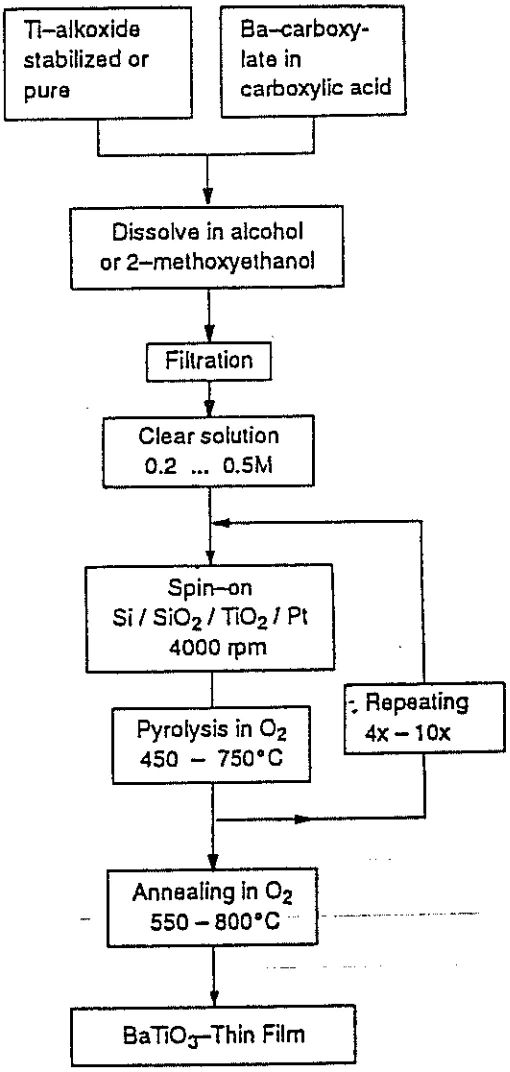

Fig. 1: CSD–processing of $BaTiO_3$ Thin Films

Results

- $BaTiO_3$ thin films were prepared by chemical solution deposition (CSD) on platinum coated silicon substrates.
- XRD analysis of films heated at temperatures > 700°C reveals a pseudocubic perovskite structure without any detectable amount of second phase.
- Different Ba–carboxylate precursors were used. The Ba–carboxylates with short alkyl chains decompose at higher temperatures than the 2–ethylhexanoates, which was investigated by IR–spectroscopy.
- SEM analysis shows that the films derived from carboxylates with long alkyl chains consist of smaller grains than the films which are derived from Ba–acetates or –propionates. This is in agreement with the lower permittivity which was measured for the $BaTiO_3$ films derived from the 2–ethylhexanoate precursor.
- The effect of a monomeric or oligomeric Ti–compound was investigated for solutions of pure titanium alkoxide precursors versus stabilizied Ti–alkoxides.

  Films derived from stabilized alkoxides exhibit strongly agglomerated grains which result in a higher dielectric constant compared to the films from the pure Ti–alkoxide.
- Dense $BaTiO_3$ thin films with grain sizes in the range of 60 nm and high dielectric constants were obtained from spin–on solutions with concentrations up to 0.3 molar. Films grown from a 0.5 molar solution exhibit a higher porosity and a lower dielectric constant.
- Crystallization studies show, that films derived from Ba–acetate or –propionate precursors crystallize via an intermediate phase, which is stable between 550°C and 650°C.
- Pyrolysis of each coating at a temperature of 450°C and sintering of the whole film at 750°C results in a fine grained $BaTiO_3$ thin film with low permittivity compared to films heated at 750°C.
- All the $BaTiO_3$ thin films show a slightly negative temperature coefficient of the permittivity. None of the films show a P(E)–hysteresis.

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ANNUAL REPORT 1995

RELIABILITY OF FERROELECTRIC THIN FILMS

Contribution:

Sol-Gel Processing of Thin Films with Ferroelectric or Conducting Properties

of the
COST 514 EU Concerted Action
"Ferroelectric Thin Films"

Institution: "Jožef Stefan" Institute, University of Ljubljana, Slovenia

Authors: M. Kosec, B. Malič, U. Delalut, G. Dražič

Ljubljana, April 1996

SF:c514-r95.doc

Objective:

To improve the reliability of PZT based thin films through the better understanding and optimisation of the solution processing.

Results:

An attempt has been made to modify the precursor system based on Pb acetate, Ti and Zr alkoxide in methoxyethanol. Lead acetate was tried to be replaced by lead oxide. From the point of ligand chemistry Pb alkoxide would be better choice as compared to Pb acetate. However, Pb alkoxides are characterised by the pure stability and have to be synthesised in situ. As reported, alkoxide of non-metal elements can be synthesised from oxides. Since lead has weak metallic character we assumed that lead oxide might be used for synthesis of alkoxides.

We found that lead oxide dissolves in methoxyethanol with the reaction of Zr and Ti n-propoxide. It forms stable, spinable solution. Amorphous precursor crystallises via pyrochlore to perovskite at temperatures common to acetate derived films. Rapid annealing of PbO based films results in fine grain microstructure with minor amount of pyrochlore, whereas acetate films processed under identical conditions exhibit rosette type microstructure with residual pyrochlore, as found by TEM. The difference in microstructure is explained by the difference in nucleation rate. PZT 53/47 PbO based films on Pt/Si substrates are characterised by well saturated hysteresis loop, Pr 12 $\mu C/cm^2$ and E_c 90 kV/cm. Film was sent to EPFL for further characterisation.

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Related activities and cooperation

Due to the limited financing of the ferroelectric thin film topic within National Research Programme of Slovenia in 1995 we had to temporarily stop the investigation of PLZT thin films we started in 1994 (see report on 1994). However, the study is continuing now within Copernicus project ERB CIPA CT 940 236 and within the new research project of Ministry for Science and Technology of the Republic of Slovenia.

Dr. Barbara Malič from the Jožef Stefan Institute has been working as a post doc for a half a year with École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, on the processing and characterisation of ferroelectric thin films. Her work is financed by the National Science Foundation of Slovenia and EPFL, Lausanne.

COST 514 : Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

Project Partners :
IMEC, Belgium (B2)
VITO, Belgium (B3)
MTI, Italy (I1)
Univ.of Pisa, Italy (I2)
EPFL, Switzerland (CH2)

Collaboration Activities Yearly Report
D.Wouters, February 1996

1. Collaboration IMEC-VITO

For the investigation of Ru and RuO_2 sputtered films as bottom electrodes for the FECAP fabrication, VITO studied the sputter deposition of these films, and deposited films on top of IMEC susbstrates for further processing by IMEC. IMEC subsequently performed heat treatments and PZT deposition tests, and electrically evaluated the properties of FECAP's made on this bottom structure.

2. Collaboration VITO-MTI

VITO also deposited RuO_2 layers on Maspec's substrates. These were returned to MASPEC for further evaluation and FECAP fabrication.

3. Collaboration MTI-Univ.of Pisa

These collaboration included : the preparation of targets, electrical analysis through measurements of the hysteresis loops for ferroelectric films and multilayers, structural analysis through X-ray diffraction, and morphological analysis through SEM.

4. Collaboration EPFL and MASPEC

Optical measuremetns of lithium tantalate thin films on glass or sapphire substrates in exchange of metal oxide depositions.

COST 514 : Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

IMEC Activities Yearly Report
D.Wouters, February 1996

TASK 1. STUDY AND OPTIMIZATION OF Pt ELECTRODES FOR USE IN SOL-GEL PZT FECAPS.

The first year, the Pt/Ti electrode structure (on top of oxidized Si substrates) was investigated. It was found that a high-temperatue bottom-electrode anneal was mandatory to get well-nucleated, single-phase perovskite PZT films on top of this bottom electrode structure. The beneficial effect of this bottom electrode annealing is explained by the diffusion of Ti through the Pt top electtrode, forming TiO_x at the surface. This TiO_x is dissolved in the spin-deposited (amorphous) PZT layer during the heat treatments, resulting in locally Ti-enriched PZT. Such high-Ti content PZT is indeed known to nucleate easily on the Pt electrode.

This procedure is, however, not feasible for making direct contacts, as e.g. the underlying Ti becomes fully oxidized, too, forming a barrier for vertical current flow. Therefore, another procedure was investigated to create the nucleation-enhancing TiO_x on top of the Pt electrode, by the spin-deposition of a thin sol-gel TiO_2 layer on this Pt bottom electrode. By varying the solvent concentration in the chemical precursor, the thickness of this TiO_2 layer could be varied in a controllable way. Good nucleation of PZT layers that still grow heteroepitaxially on top of the (111) oriented Pt could thus be obtained. This method makes it possible to make good quality PZT films independently of the sub-Pt bottom electrode structure.

TASK 2. INVESTIGATION OF Ru AS ELECTRODE MATERIAL

By the VITO, Ru and RuO_2 thin electrode films were sputter-deposited on our substrates.

Oxidation of the Ru films in order to make RuO_2, however, resulted in very rough films. The Ru-sputtered films furthermore had poor adhesion. In situ deposition of Ti layers was not possible yet due to vacuum problems of the system (together with the low sputtering rate).

In sity reactively sputtered RuO_2 films, however, could be used as bottom electrodes for the PZT deposition. Both RuO_2 films on top of Pt and TiO_2 coated samples were used. The PZT (20/80) films were spin-deposited and crystallized into single-phase perovskite, as revealed by XRD analysis. Ru top electrodes were deposited by laser ablation through a shadow mask, and converted to RuO_2 by a high-temperature anneal in O_2. The hysteresis loops of these ferroelectric capcitors were measured using a modified Sawyer-Tower circuit, and revealed high-quality rectangular loops with good saturation, and did not show (excessive) leakage current.

COST 514 : Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

VITO Activities Yearly Report
February 1996

The activities of VITO were focussed on the sputter deposition of Ti, Ru and RuO_2. A study of the sputtering process for these materials was done during a master thesis work [ref.1]. An important result is the ability to obtain crystalline RuO_2 films in situ during the reactive sputtering proces, and this without sample preheating. The preferential oreintation of the RuO_2 film was hereby depending on the oxygen partial pressure during sputtering.

Except for this study, VITO prepared a number of samples for IMEC and MASPEC which are collaborating in the project [see next page for an overview]. In regular meetings with IMEC the results were discussed and IMEC could evaluate the material for use as a bottom electrode for PZT deposition and FECAP fabrication.

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Chronological survey of r.f. sputter depositions in the framework of COST 514

Exchange of samples

date	**substrate** **(origine)**	**sputtered layers**
25/1/95	A: Si/500nm PSG B: Si/500nm PSG/10nm Ti C: Si/600nm SiO$_2$ D: Si **(IMEC)**	A, B, C and D:100nm Ru A,C and D: 10nm Ti/100nm Ru
2/3/95 8/3/95	B: Si/500nm PSG/10nm Ti A: Si/500nm PSG **(IMEC)**	B: RuO$_x$ *(Ar:O$_2$=14:1,13:2,10:5, en 7.5:7.5)* A: 10 nm Ti/RuO$_x$ *(Ar:O$_2$=14:1,13:2,10:5, en 7.5:7.5)*
4/95	Si **(MASPEC)**	RuO$_x$ 10nm Ti/RuO$_x$ *(cfr. IMEC dd. 8/3/95)*
6/12/95	PR01-04:Si/400nm SiO$_2$/10nm Ti/21nm Pt SOR01-06:Si/400nm SiO$_2$ **(IMEC)**	PR01-02:100nm Ru PR03-04: 100 m RuO$_2$ SOR01-02: 10nm Ti/100nm Ru SOR03-04: 10nm Ti/100nm RuO$_2$ SOR05-06: 10nm Ti/50nm Ru/50nm RuO$_2$

Report on COST 514 Action FERROELECTRIC CERAMIC THIN FILMS

Project: **MATERIALS FOR A FERROELECTRIC CAPACITOR STACK WITH DIRECT CONTACT TO SILICON**

Group: **Centro Interdipartimentale Materiali e Tecnologie dell'Informazione (MTI), Università di Parma, V.le delle Scienze, I-43100 PARMA, ITALY.**

B.E. Watts Istituto MASPEC/CNR, Via Chiavari 18a, I-43100 PARMA, ITALY.
Tel: +39 521 269207 Fax: +39 521 269206
email leccabue@prmasp.pr.cnr.it

1. Study of crystallisation of PZT on RuO_2 electrodes

A systematic study of the phase distribution in $PbZr_{0.52}Ti_{0.48}O_3$ films deposited, using a XeCl excimer laser, on two electrodes Si/RuO_2 and $Si/Ti/RuO_2$ has been carried out. In addition, the substrate temperature and laser fluence were changed in order to refine the growth parameters. The electrodes were given a rapid heat treatment at 600 °C for 5 min in air before depositing the PZT film.
The sputtered electrodes were provided by J. Smeets VITO (Mol) and will be the subject of two symposium presentations, presented jointly by the partners in the project.

Ferroelectric Thin Films V, MRS Symposium, S. Francisco April 1996.
E-MRS Symposium H, Strasbourg, June 4-7 1996.

2. The research into the preparation of lead zirconate titanate films by sol-gel in recent years has tended to use two different types of solvent: (i) alcohols (methoxyethanol, propandiol); (ii) fatty acids (acetic, propionic). This work has studied the effects of process variables on an acetic acid route.

Lead II acetate, zirconium butoxide and titanium propoxide were dissolved, sequentially, in glacial acetic acid. A correct dehydration of the lead acetate and low temperature mixing was found to increase the stability of the solution. Acetylacetone (acac) stabilised the solution to a great extent and water, added after all the components were mixed had a more marked effect.

The beneficial effects of acac and H_20 were also seen during the processing of the films. The solutions, spun onto platinum coated silicon substrates, were much more even coatings if they were modified. The amount of pyrochlore phase fell and the crystallisation temperature was significantly lowered.
To be presented at Electroceramics V Conference, Aveiro, 2-4 September 1996

3. The crystallisation behaviour of thin films of composition $Pb_{1.1}Zr_xTi_{1-x}0_3$ where x= 0.75 and 0.25, prepared by a sol-gel route, have been studied using grazing angle X ray diffraction and transmission electron microscopy. The X ray diffraction was done at different incident angles and revealed different structures as the penetration into the film increased. Titanium rich films were mainly perovskite with titanium oxide which may have formed within the film during

its crystallisation. The pyrochlore phase in the zirconium rich film is more evident near the surface; this is also confirmed by microscopy of the film in cross section. In addition, an irregular distribution of the titanium, used as the adhesion layer was also seen on the micrographs. The electrical measurements evidence some correlation with the micro structure observed.
A similar study has been performed on a series of samples as a function of temperature.
The work has been submitted to The Journal of Crystal Growth.

4. The fatigue measurement apparatus has been completed and improved the first results have been presented at **ECRS Conf. Riccione, Italy, Oct 2-6 1995.**

A. De Vuono, G. Chiorboli, C. Morandi, [1]B.E. Watts, [1]F. Leccabue and [2]D. Seuret
Dipartimento di Ingegneria dell'Informazione, Università di Parma, 43100 Parma, Italia

[1]Istituto MASPEC/CNR, Via Chiavari 18A, 43100 Parma, Italia

[2]Facoltà di Fisica, Universita dell'Avana, Cuba.

In this paper an apparatus to measure the degradation of the pulsed hysteresis caused by fatigue is described, along with the various features of the equipment which were adopted in order to fatigue a bank of 16 ferroelectric capacitors, at variable frequencies up to 2.5 MHz. Preliminary results obtained on a film of $Pb_{1.1}Ti_{0.48}Zr_{0.52}O_3$ are also presented.

Dipartimento di Fisica
Università di Pisa
Piazza Torricelli 2
56126 - PISA (Italy)

Tel.: +39-50-911244
+39-50-911111 (operator)
FAX: +39-50-48277

TELEFAX MESSAGE

Destination telefax: 0032 16 281501 Date: 15/2/96

TO: DR. DIRK WOUTERS - IMEC LOVANIO

FROM: Francesco Fuso / Allegrini

Pages following: 1

Re: COST 514

Dear Dr. Wouters,

here following please find some information on our 1995 activity within the COST514 action.

We will not participate to the forthcoming COST meeting; anyway Dr. Watts from MASPEC - Parma will bring with him our material (one-year report and other information).

Looking forward to hearing from you again

Best regards

Francesco Fuso

Information on COST514 activity in 1995

Unità INFM, Dipartimento di Fisica, Università di Pisa, Piazza Torricelli 2, I-56126 Pisa (Italy), tel. +39 50 911 244, fax +39 50 48277, e-mail: allegrin@ipifidpt.difi.unipi.it

Group composition:
E. Arimondo, M. Allegrini, F. Fuso, M. Labardi, F. Lazzeri, A. Iembo, L. Ceresara

Activity:

Pulsed laser ablation and deposition of ferroelectric PZT thin films and multilayer structures $Si/SiO_2/RuO_2/PZT$ and $TiSrO_3/YBCO/PZT$. Structural (X-ray diffraction, SEM and TEM), stoichiometric (XPS) and functional (hysteresis loop) characterization on RuO_2 films and multilayer structures.

Interaction with other partners in the COST514 action:
Collaboration with the group in Parma (MASPEC/CNR): preparation of targets, electrical analysis through measurements of the hysteresis loop for ferroelectric films and multilayers, structural analysis through X-ray diffraction, morphological analysis through SEM

Relevant publications in the field covered by the COST 514 action in 1995:

1. M. Labardi, M. Allegrini, F. Fuso, F. Leccabue, B. E. Watts, C. Ascoli and C. Frediani, *"Scanning and Friction Force Microscopy (SFFM) of ferroelectric $Pb(Zr,Ti)O_3$ thin films"*, Integr. Ferroelectr. 8, 143 (1995)

2. S. Amoruso, V. Berardi, N. Spinelli, R. Velotta, M. Armenante, F. Fuso, M. Allegrini and E. Arimondo, *"Time-of-Flight Mass Spectrometry and Covariance Mapping Technique Investigation of Charged Species Evolution in $Pb(Ti_{0.48}Zr_{0.52})O_3$ Laser Ablation"*, Appl. Surf. Sci. **86**, 35 (1995)

3. S. Amoruso, V. Berardi, N. Spinelli, R. Velotta, M. Armenante, F. Fuso, M. Allegrini and E. Arimondo, *"Laser Ablation of $Pb(Ti_{0.48}Zr_{0.52})O_3$ Target: Characterization and Evolution of Charged Species"*, J. Appl. Phys. **78**, 494 (1995)

4. V.A.. Yakovlev, G. Mattei, A. Iembo, F. Fuso, E. Arimondo, M. Allegrini, F. Leccabue and B.E. Watts, *"Raman and Infrared Spectroscopy of Ferroelectric $Pb(Zr_{0.48}Ti_{0.52})O_3$ Films Deposited by Pulsed Laser Ablation"*, J. Appl. Phys. **78**, 6321 (1995)

5. A. Iembo, F. Fuso, E. Arimondo, C. Ciofi, G. Pennelli, G.M. Currò, F. Neri and M. Allegrini, *"Pulsed Laser Deposition and Characterization of Conductive RuO_2 Thin Films"*, J. Mater. Res., in press

6. *"Pulsed laser ablation deposition and characterization of superconductive/ferroelectric multilayers"*, to be submitted to Supercond. Sci. Technol.

7. *"Structural characterization of RuO_2/PZT multilayers deposited by pulsed laser ablation"*, in preparation

INSTITUT DE PHYSIQUE APPLIQUÉE

DÉPARTEMENT DE PHYSIQUE

PHB Ecublens CH-1015 LAUSANNE Suisse
Téléphone: +41 (0)21 - 693 11 11
Téléfax: +41 (0)21 - 693 46 66 TÉLEX: 454 478

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

COST 514 : FERROELECTRIC CERAMIC THIN FILMS
ONE-YEAR REPORT/March 96

C.-H. Kohli, X. X. Qu, P. E. Schmid and F. Lévy

Institut de Physique Appliquée,
Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne (Switzerland)

1. Lithium tantalate thin films

1.1 Sample preparation

Lithium tantalate thin films have been successfully deposited on RuO_2-coated silicon substrate. Thin films are deposited by reactive RF sputtering from ceramic target. The deposited films are amorphous, and different thicknesses from 50 nm to 400 nm are deposited.

The deposited films are crystallised after a rapid thermal annealing (RTA) during 45 s at 600°C in an O_2 atmosphere.

1.2 Film characterisation

Structural characterisations are carried out by X-ray diffraction (XRD), by scanning electron microscopy (SEM), and by transmission electron microscopy (TEM), in particular in cross-sectional samples. Grazing incidence (5°) X-ray diffraction shows that the crystallised phase is obtained after a thermal treatment at 500°C. The films are polycrystalline. SEM and TEM observations show grain size of about 200 nm.

Investigations by secondary ion mass spectrometry (SIMS) show Ta and Li diffusions into the Si substrate down to 50 nm. These diffusions can be prevented with a 100 nm thick SiO_2 interlayer.

1.3 Electrical characterisation

The electrical measurements are carried out in the sandwich configuration (an upper electrode is evaporated or sputtered onto the lithium tantalate films deposited on RuO_2-coated silicon substrate), with Au, Ni or RuO_2 circular upper electrodes. The film resistivity and the relative permittivity are measured with an impedance analyser. At 1 kHz and room temperature, the resistivity is 3×10^8 Ωcm and the permittivity is 30 for device with Au upper electrode. With Ni upper electrode, the resistivity is 2×10^8 Ωcm and the permittivity is 33. For a device with RuO_2 upper electrode, the resistivity is 7×10^8 Ωcm and the permittivity 35.

Measurement of the permittivity as a function of the temperature shows an increase of the permittivity with the temperature. The permittivity reaches a maximum value between 590 and 610°C (Curie Temperature).

The pyroelectric coefficient is measured by the quasi-static method[1]. A pyroelectric coefficient of the order of 70 μC/m^{2}K is obtained at room temperature.

2. SbNbO$_4$ thin films

SbNbO$_4$ thin films are deposited on Pt-coated silicon substrates at room temperature by ion-beam sputtering. The as-deposited films are amorphous and a post-treatment by RTA in an Ar atmosphere is carried out to reach the crystallised ferroelectric SbNbO$_4$ phase.

X-ray diffraction spectra of SbNbO$_4$ thin films and ceramics indicate that the film is textured with a preferential orientation of the (040) planes parallel with the substrate surface. The average size of SbNbO$_4$ crystallites is of the order of 100 nm.

0.6 mm diameter Au upper electrodes are evaporated onto the SbNbO$_4$ films for electrical measurement. The dielectric permittivity and loss are measured by using an impedance analyser. At 10 kHz, the dielectric permittivity and the loss factor are 45 and 0.07, respectively.

The electric field dependence of the polarisation for a film about 400 nm in thickness is measured with the help of a modified Sawyer-Tower circuit. The remanent spontaneous polarisation and the coercive field are 0.65 μC/cm^2 and 43 kV/cm, respectively.

3. Reference

1. N. P. Hartley, P. T. Squire and E. H. Putley, J. Phys E: Sci. Inst. 5 (1972) 787.

4. Publications

1. C.-H. Kohli, J. Moser, K. Prasad, P. E. Schmid, F. Lévy and G. Burri, "Characterization of lithium tantalate thin films sputter-deposited onto RuO$_2$/Si substrates", Microelectronic Engineering 29 (1995) 201-204.
2. X. X. Qu and F. Lévy, "Textured ferroelectric SbNbO$_4$ thin films deposited by ion-beam sputtering", Ferroelectric Letters 20 (1995) 83-88.

5. Collaborations

- Prof. N. Setter, Dr. P. Muralt, LC-DMX-EPFL, Lausanne/Switzerland: RTA, ferroelectric, pyroelectric measurement and infrared spectroscopy.
- Dr. B. Watts, MASPEC-CNR, Parma/Italy: Optical measurements of lithium tantalate thin films on glass or sapphire substrates in exchange of metal oxide depositions.

Distribution:

- Dr. D. Wouters, IMEC, Leuven/Belgium.
- Dr. B. Watts, MASPEC-CNR, Parma/Italy.
- Prof. N. Setter, LC-DMX-EPFL, Lausanne/Switzerland.
- Dr. L. Pardo, ICMM-CSIC, Madrid/Spain.

Microelectronics and Material Physics Laboratories
University of Oulu,
PL 400, FIN-90571 Oulu, Finland.

COST 514 Program	Report of activities in 1995
Title of the project	Pulsed laser ablation deposition of ferroelectric thin films
Project leader	Prof. S. Leppävuori
Group members	J. Levoska, T. Murtoniemi,J. Lappalainen

Summary

Pulsed laser ablation deposition of PZT and conducting oxide electrodes (includig high Tc superconductors) and their heterostructures by an *in situ* process has been studied, and the structure and properties of the films and heterostructures have been characterized.The latest studies have been concentrated on the deposition of oxide electrodes and PZT on silicon using yttrium-stabilised zirconia buffer layers. The studies of post-annealed polycrystalline PZT films has been continued.

Scientific results

Layered thin film structures containing ferroelectric Nd doped lead zirconate titanate (PZT) and conducting lanthanum strontium cobalt oxide (LSCO) or high Tc superconducting $YBa_2Cu_3O_{7-d}$ (YBCO) compound were deposited in an *in situ* process by pulsed laser ablation using an XeCl excimer laser and sintered polycrystalline targets. The structures were grown on heated strontium titanate (STO) (100) and MgO (100) single crystal substrates and on epitaxial laser ablated yttrium-stabilized zirconia (YSZ) buffer layers on Si (100) and silicon-on-sapphire (SOS).

The structure, orientation relationships and degree of epitaxy and crystal perfection of the films were studied by X-ray diffraction, scanning electron microscopy (SEM) and micro-Raman specroscopy. Good crystal perfection, phase purity and epitaxy of (001) oriented trigonal PZT was obtained on STO substrates and on c-axis oriented epitaxial YBCO films deposited on STO substrates and on epitaxial LSCO deposited on STO and MgO. On the films on YBCO/YSZ/Si (or SOS), both (100) and (110) oriented PZT was observed. In the latest experiments, it was found that (110) oriented PZT can be grown on LSCO/YSZ/Si under proper conditions.

Capacitor structures were were fabricated using masking during the deposition. Laser ablated Pt top electrodes were used. Ferroelectric properties of PZT films and resistive properties of the structures were measured both at room temperature and cryogenic temperatures. For the films on YBCO and LSCO electrodes on STO and MgO, the maximum polarization at an electric field of 220 kV/cm was 30 and $\mu C/cm^2$, the remanent polarization 16 and18 $\mu C/cm^2$ and the coercive field 77 and 62 kV/cm, respectively. For the films on Si and SOS, cracks were formrd during cooling, making the measurements of ferroelectric properties difficult.

Polycrystalline PZT films were deposited at room temperature on laser ablated Pt electrodes on MgO and Si and post-annealed at 650 - 675°C. Dielectric constants and loss angles were measured as a function of film thickness. From hysteresis measurements, the remanent polarisation was found to be 18 $\mu C/cm^2$ in the films deposited on MgO but generally much lower in films deposited on Si. The electrical conductivity of the films were studied as a function of temperature, and Poole-Frenkel was found to be the most obvious mechanism responsible for long term leakage currents. Macroscopic mechanical stresses in PZT films were studied by x-ray diffraction. In films on MgO, compressive stress (about 200 MPa) was found, on Si, tensile stress (about 300 MPa) was measured.

Publications

J. Hagberg, J. Levoska, S. Leppävuori, T. Murtoniemi, Y-Ba-Cu-O/PZT distributed RC-element, Mat. Res. Soc. Symp. Proc. 361 (1995) 607-612.

J. Lappalainen, J. Frantti, H. Moilanen, S. Leppävuori, Excimer laser ablation of PZT thin films on silicon cantilever beams, Sensors and Actuators, 46-47 (1995), 104-108.

H.X. Zhang, S. Leppävuori, P. Karjalainen, Raman features in laser ablated PZT thin films near the morphotropic phase boundary, J.Appl. Phys. 77 (1995) 2691-2696.

J. Lappalainen, J. Frantti, S. Leppävuori, Characterization of post-annealed PZT thin films deposited using pulsed laser ablation, Mat. Res.Soc. Symp. Proc. 361 (1995) 581-586.

J. Levoska, T. Murtoniemi, J. Lappalainen, S. Leppävuori, Deposition of epitaxial ferroelectric lead zirconate titanate and conducting oxide electrodes by pulsed laser ablation, accepted for publication in Ferroelectrics.

COST514 EU Action
Group of projects : "Ferroelectric Thin Films for SAW devices"
1995 Report of Activities

The following collaborative activities were carried out during 1995:

Incorporation of Dr. Etienne Snoeck (CEMES-LOE, France) project to the group, implementing the task of compositional and structural analysis of the samples by high resolution EDS of X-rays and TEM.

Short Term Scientific Missions were carried out by:

- Dr. Jesús Ricote (July 95)- presently at Cranfield Univ. (UK) - for the TEM study of Sm-modified lead titanate samples, processed by sol-gel route, which gave place to the results presented by Dr.Snoeck at the COST514 Workshop'96.
- Mr. Miguel Algueró (Sept. 95) at EPFL to attend a workshop on "Materials Technology for Ferroelectric Microsensors, Microactuators and Micoelectronic Components" and to carry out some preliminary piezoelectric and pyroelectric measurements on modified lead titanate samples.

The following main topics were those aimed during 1995:

- Microstructure control by control of the processing parameters in the sol-gel route.
- High resolution microstructural study of the sol-gel samples by HRTEM, EDS,UPS and RBS.
- Study of the ferroelectric behaviour of the sol-gel samples.
- Development of modified lead titanate thin films by PLD and electrical characterization.

All this resulted in an enhancement of the microstructural and electrical properties control of the films , that it is expected to give place to enhanced functional properties, that could be tested in a near future by Manchester University. New compositions could be now developed by PLD from ceramic targets provided by Ferroperm.

The results of these activites are shown in the following works:

* Presented in the COST514 Workshop'96 :

- "Ferroelectric characterization of sol-gel modified $PbTiO_3$ FTF". Prof. J. Mendiola.
- "TEM Studies on Sol-Gel Processed Modified Lead Titanate Thin Films" Dr. E. Snoeck.
- "Processing Parameters affecting the Properties of Sol-Gel derived Modified Lead Titanate Thin Films". Dra. M. L. Calzada.
- "Pulsed laser deposition and electrical characterization of ca-modified lead titanate thin films"

Dr. C. Zaldo.

* Other:

- "Quantitative study of the microstructure of Sm substituted lead titanate thin films".

L. Pardo, J. Ricote, R. Sirera and M.L. Calzada.
Microelectronic Engineering 29, 301-304 (1995).

- "Structure and ferroelectric properties dependence on thermal treatment of modified lead titanate thin films". J. Mendiola, M.L. Calzada, R. Sirera and P. Ramos.

Journal of Materials Science 31, 617-623 (1996).

PREPARATION AND CHARACTERIZATION OF FERROELECTRIC THIN FILMS BY SOL-GEL PROCESSING

Macit ÖZENBAŞ

Department of Metallurgical Engineering
Middle East Technical University
Ankara, 06531 Turkey

The present work describes the preparation of $Pb(Zr,Ti)O_3$ thin films and powders from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

In recent years, preparation and synthesis conditions of uniform and chemically homogeneous particles of ferroelectric ceramics have been investigated by numerous researchers using sol-gel alkoxides, hydrothermal synthesis, and co-precipitation techniques. There might be one other possibility for the synthesis of fine, monosized and agglomerate-free powders of PZT, PLZT, etc. compositions, namely homogeneous precipitation from aqueous solutions. This method involves the reaction of nitrates, chlorides, or acetates of the cations desired in the final composition, in the presence of urea $[(NH_2)_2CO]$ in an aqueous solution in the temperature range 75-98°C to produce the precursors in a few hours. Urea, which slowly decomposes to yield ammonia and HNCO, in situ, is used as the ligand source for ammonia.

EXPERIMENTAL PROCEDURE

The materials used for homogeneous precipitation are basically :

- $ZrCl_4$
- $TiCl_4$
- $PbCl_2$
- Urea

The concentrations studied are given below :

Pb^{+2} .... 0.001 - 0.005 M
Zr^{+4}, Ti^{+4}, Urea .... 0.1 - 0.5 M

The process involved :

- Addition of stock solutions in proper amounts to form the desired compound at the end, together with urea in sufficient water in order to obtain a clear solution.
- Ammonium hydroxide was used to regulate the pH of the solutions.
- The resulting PZT precursors were gelled by holding at 90°C for 1 to 2 h while magnetically stirring.
- The starting pH of the precursors was between 0 and 1.
- However, the pH gradually increased to 5-5.5 due to ammonium hydroxide addition at the gelation temperature and a white precipitate formed in the solution.
- These precipitates were dried at 120°C for 5-6 h in an oven.
- They were fired at 350°C, 650°C, and 850°C for 5, 5, and 3 h, respectively, in the oxygen atmosphere to obtain polycrystalline powders.

The substrate materials for the films are

- silicon (111) wafers
- α-Al_2O_3.

- The coating of the films was accomplished by dipping the substrates into the coating solutions, which were obtained from the precursors used for the powder formation.
- The heat treatment conditions for the decomposition of residual organics in the films were determined on the basis of thermal analyses of the bulk gels.
- The coated films were dried at around 100°C for 10 min.
- The above process should be repeated in order to increase the thickness of the films.
- A film of approximately 0.2 µm thick was deposited in a single process and the final film thicknesses determined by SEM were about 1.1-1.2 µm.
- Finally, the films were annealed at 350°C, 650°C, and 850°C for 3 h in open alumina crucibles in the oxygen atmosphere to obtain crystallization.
- The heating and cooling rates used were 20°C/min and 1.5°C/min, respectively.
- The particle size, the morphology and the film surfaces were observed from SEM (Jeol-JSM 6400) micrographs.
- EDX analyses were carried out on the same samples to give information on the composition of the films.
- XRD investigations were performed with a Philips diffractometer.

RESULTS

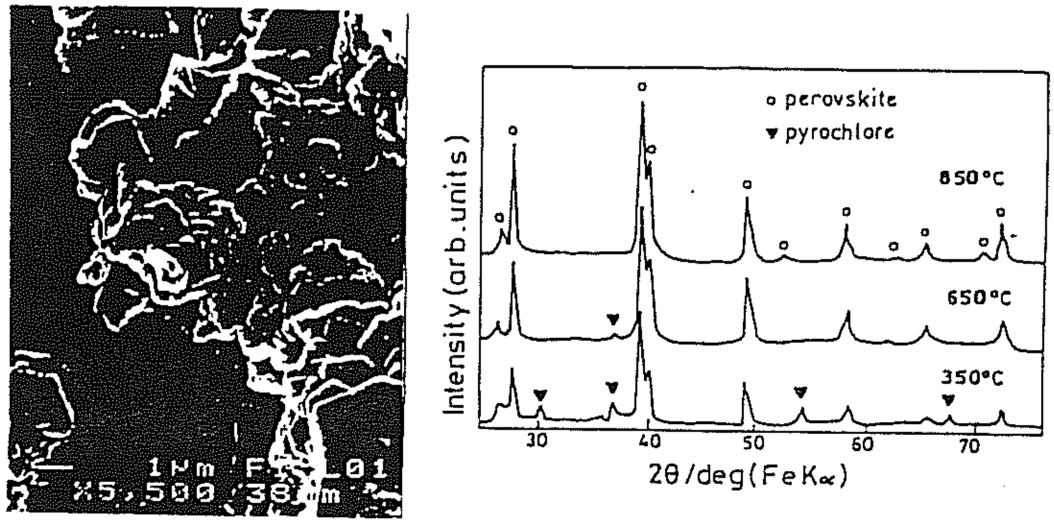
PZT Powders

- For the observation of powders, small amounts of the suspensions were rapidly dried by heating on common SEM sample holders, the surface of which had additionally been polished to less than 0.5µm surface roughness.

•The particles of PZT composition obtained by using urea yielded particle sizes from submicron range to a few microns (Figure 1.a).
•The particles of the same composition obtained without the use of urea were about 50-100 µm in size.
•The use of the homogeneous precipitation process leads to micron-sized particles with high homogeneity and possibly gives films with better physical properties.
•Conversion of the precipitated amorphous powders to the PZT oxide phase was evaluated by X-ray diffraction.
•XRD studies show that the crystallization started around 350°C.
•Heat treatment at 650°C decreased the amount of pyrochlore phase and finally at 850°C, the sample was all perovskite phase (Figure 1.b).
•This temperature is especially important for lead-containing systems to avoid the PbO loss problem during heat treatment.
•The crystal structure appeared to transform from pseudocubic to tetragonal with increasing temperature, and the original composition was slightly to the tetragonal side of the morphotrophic phase boundary.
•The enhanced definition of tetragonal splitting, with increased intensity at higher temperatures, indicates a greater degree of crystallinity for material heat-treated at these temperatures.
•The lattice parameters for the gel-derived powders agree with those of the sintered samples, which indicates that the chemical composition of the gel-derived powders does not deviate much from that of the starting solutions.

PZT Films

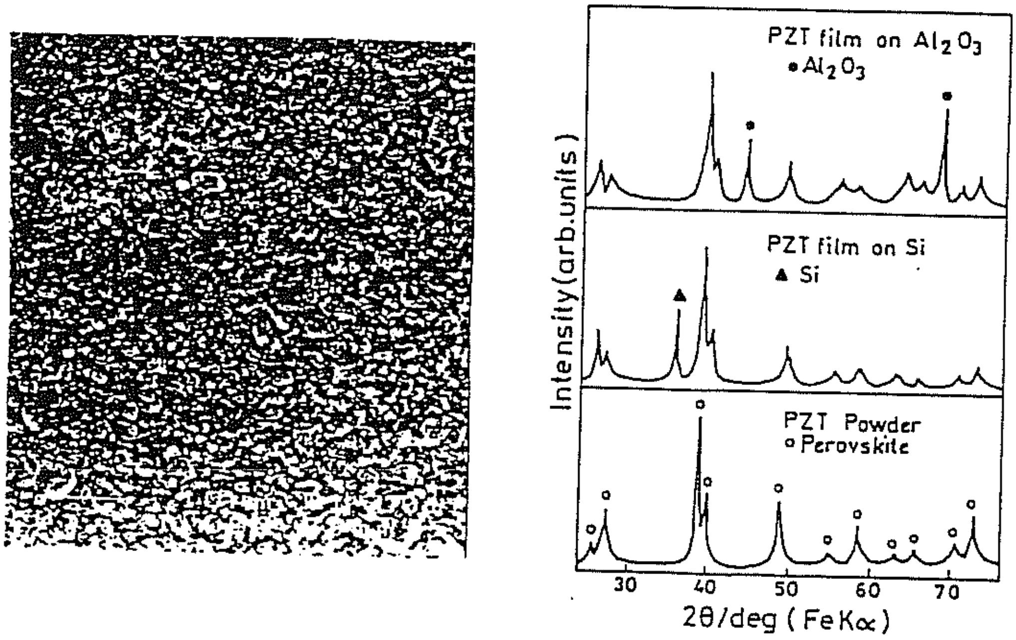
•The resulting crystal structure of sol-gel derived PZT thin films was highly sensitive to both the initial chemical composition and heat treatment temperature.
•In general, it was found that the crystallization process was somewhat retarded in films as compared with powder samples. Sol-gel derived powder samples crystallized at temperatures approximately 50°C lower than corresponding thin film samples.
•The development of the initial pyrochlore phase was observed during the thermal processing of thin films. The volume fraction of the pyrochlore phase and the time required for its transformation to the perovskite phase were strongly temperature dependent.
•In general, heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated. XRD analyses showed that films of 1.1-1.2 µm thickness were polycrystalline with no preferred crystallographic orientation (Figure 2).



a

b

Figure 1. (a) Scanning electron micrograph of sol-gel derived PZT particles obtained by using urea. (b) XRD patterns of PZT powders for different heat treatment temperatures.



a

b

Figure 2. (a) Scanning electron micrograph of the PZT film surface on alumina substrate, heat treated at 850°C for 3 h. (b) XRD patterns of the films on alumina and silicon substrates.

Meetings Attended in 1995 :

1. M. Özenbas, "Preparation and Characterization of Ferroelectric Thin Films by Sol-Gel Processing Using Urea", Ferroelectric Thin Films Workshop, February 16-17, 1995, Lausanne, Switzerland.

2. M. Özenbas and Ü. Ergin, "Preparation of $Pb(Zr,Ti)O_3$ Thin Films and Powders by the Sol-Gel Process", 8th European Conference on Ferroelectricity, July 4-8, 1995, Nijmegen, The Netherlands (Paper will be published in *Ferroelectrics*).

3. Ü. Ergin and M. Özenbas, "Preparation and Characterization of Ferroelectric Thin Films", 12th National Congress on Electron Microscope, September 11-15, 1995, Antalya, Turkey.

Thesis Offered in 1995 :

1. Ü. Ergin, "Preparation and Characterization of Ferroelectric Thin Films by Sol-Gel Processing", M.Sc. Thesis, Dept. of Metallurgical Eng., Middle East Technical University, Ankara, Turkey (continuing).

European Commission

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COST 514

Ferroelectric ceramic thin films

Annual report 1996

Edited by

Dr. Lorena Pardo (chairperson)
Peter Lobotka (scientific secretary)

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Contents

Summary of activities in the year 1996

COST 514 - Ferroelectric Thin Films

Group project : Reliability of Ferroelectric Thin Films

Participants :

B1:	IMEC, Division MAT-ARS, Leuven, Belgium Dr. D. Wouters (IMEC)
CH1:	EPFL, Laboratoire de Céramique, Lausanne, Switzerland, Prof. N. Setter (EPFL)
D1 :	RWTH Aachen, Institut für Werkstoffe der Elektrotechnik, Aachen, Germany Prof. Dr. Waser (RWTH)
SLO1:	"Jozef Stefan" Institute, Ljubljana, Slovenia Dr. M. Kosec (JSI)
UK4:	University of Sheffield, Dept. of Engineering Materials, Sheffield, England, Dr. W. Lee and Dr. I. M. Reaney (Sheffield)

The activities within the group project are summarised as follows, whereas the details are described in the reports of the individual groups.

The topics studied :

- Endurance of Pt-electroded PZT ferroelectric capacitors; influence of film orientation (IMEC)
- Piezoelectric properties of sputtered and CSD derived PZT thin films as a function of Zr/Ti ratio and thickness of the films (EPFL)
- Self-polarization effect of PZT thin films versus composition, bottom electrode, post annealing, and film thickness (EPFL)
- Comparative study of piezoelectric and dielectric ageing in PZT thin films and bulk ceramics (EPFL)
- Influence of poling fields and poling temperature on the piezoelectric properties of CSD PZT thin films (EPFL)
- Piezoelectric properties of $SrBi_2Ta_2O_9$ (SBT) thin films (EPFL)
- Electromechanical properties of CSD $Pb_{1-x}Ca_xTiO_3$ (PCT) films (EPFL-CSIC Madrid)
- Effect of ferroelectric polarization on the transient current response of PZT thin films (RWTH-EPFL)
- Dielectric properties, leakage behaviour, and resistance degradation of thin films of the $Ba(Ti_{1-Y}Zr_Y)O_3$ solid solution series (RWTH)
- The effect of alkoxide precursor structure of Ti and Zr on the crystallization and microstructure of PZT based thin films prepared by the methoxy ethanol route (JSI)

- Influence of lanthanum precursor and excess lead oxide on the pyrolysis, crystallization, microstructure and properties of PLZT films processed by the acetic acid route (JSI-EPFL)
- TEM study of various thin films: sputtered $PbTiO_3$ films on RnO_2 or Pt. CSD films prepared by single or multiple coating, fatigued and nonfatigued films (Sheffield-EPFL)

Exchange of scientists, visits

- Post-doctoral fellowship. Dr. Barbara Malič, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique: 15.1. - 15.7.1996 Topic: Processing and characterization of PLZT Thin Films.
- Short Term Sci. Mission, Dr. Barbara Malič, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, 18. - 29.11.1996, Research on PLZT thin films
- Visit, Dr. Marija Kosec, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, 23.11.1996.
- Visit, Dr. Marija Kosec, Institut für Werkstoffe der Electrotechnik RWTH Aachen, 7.-8.11.1996.
- Short term Sci., Mission, Dr. Ian M. Reaney, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, 11. - 23.8.1996, TEM study of ferroelectric thin films.

COST 514: Reliability of Ferroelectric Thin Films

IMEC Activities Yearly Report
D.Wouters, April 1997

Study of the endurance of Pt-electroded PZT ferroelectric capacitors

The endurance of Pt-electroded PZT FECAPs was studied using samples with different orientation of the PZT film. As mentioned in the previous yearly report, we are able to control the orientation of the PZT films deposited by sol-gel technique on Pt/Ti/SiO2/Si substrates. Depending on the processing and temperature treatment of the bottom-electrode-substrate structure, either very strong (111) or very strong (100) preferential oriented films are obtained (the orientation is for the high-temperature cubic state).

For the highly (111) oriented films, very rectangular hystersis loops are obtained, with high Pr. However, very strong fatigue is observed staring already around 10^4-10^5 cycles.

For the highly (100) oriented films, the hysteresis loops are less steep, a nd Pr is reduced. However, (i) better fatigue characteristics are obtained, and (ii) because of the less abrupt switching, it is possible to operate these FECAPs in the unsaturated switching regime using lower switching voltages. In this regime, excellent fatigue resistance is obtained up to 10^{11} cycles, however at reduced signal (Pr).

The difference in fatigue behavior is explained by the difference in switching mechanisms in (111) vs. (100) oriented films, being 180° "bulk" switching for (111) films and 90° lateral domain wall switching in (100) oriented films. The bulk switching mechnaism is much more abrupt and will result in much larger field variations at the PZT-electrode interface, wich can lead to increased carrier injection and/or damage.

A summary of thisd study can be found in " Influence of the ferroelcectric domain structure and switching properties on the endurance of PZT ferroelectric capacitors", D.JWouters and H.E.Maes, Microelectron. reliab., Vol.36, No.11/12, p.1763-1766, 1996.

Laboratoire de Céramique
Ecole Polytechnique Fédérale de Lausanne
Switzerland

Annual report 1996

of the project

Reliability of Ferroelectric Thin Films

Contribution

Degradation Phenomena in Electromechanical Properties of Ferroelectric Thin Films

of the
COST 514 EU Concerted Action
"Ferroelectric Thin Films"

Author: A. Kholkin

Purpose of the project

Characterization of the electromechanical activity of ferroelectric thin films deposited by different techniques (sol-gel and magnetron sputtering) and investigation of the degradation mechanisms of the electromechanical response

Main results:

1. Piezoelectric coefficients (d_{33}) and strains were investigated for a wide range of $PbZr_xTi_{1-x}O_3$ compositions from x=0.1 (tetragonal) to x=0.7 (rhombohedral) prepared by magnetron sputtering and sol-gel techniques. A distinct maximum of d_{33} and strain as a function of the composition was observed in accordance with bulk ceramics data. The d_{33} maximum for sputtered films was shifted to the tetragonal side of the phase diagram as compared to that in bulk ceramics. Typically, the sol-gel films exhibited better piezoelectric properties than sputtered films mainly due to the higher dielectric permittivities.

An ac field and frequency effects on piezoelectric response of poled films were investigated for several selected PZT compositions. The piezoelectric coefficients were relatively independent on driving field in tetragonal films while strong ac effect was found for MPB composition. This behavior was explained in terms of the domain wall motion contribution to the piezoelectric response.

A strong dependence of the piezoelectric response on the preferred orientation was found in PZT 70/30 films. (100) oriented films showed better piezoelectric properties than (111) films in agreement with phenomenological calculations taking into account the clamping effect of the substrate.

A thickness dependence of the piezoelectric properties was studied in PZT 45/55 films prepared by sol-gel technique. Significant increase of d_{33} with thickness was associated with a smaller influence of interface layers and/or with a reduction of the internal stresses in thicker films.

Both sol-gel and sputtered films exhibited an initial piezoelectric activity for virgin films (self-polarization effect). This effect was studied as a function of the PZT composition, bottom electrode material, postannealing temperature, and film's thickness. For films having no additional postanneal the initial d_{33} could be more than 80% of that obtained by subsequent poling. A plausible explanation of self-polarization effect in ferroelectric thin films was proposed.

2. A comparison study of piezoelectric and dielectric aging was performed in PZT 45/55 thin films and bulk ceramics. It was found that piezoelectric aging in thin films obeys the logarithmic time dependence with a relative aging rate much higher than that of the dielectric constant, while comparable aging rates were found in PZT ceramics. The origin of piezoelectric aging was related to depolarization of the films rather than to suppression of the domain wall motion as was generally accepted for PZT ceramics. This conclusion was confirmed by the comparison of d_{33} aging with polarization retention after the same poling conditions and by the frequency and ac field dependences of piezoelectric aging.

3. The influence of the poling field, poling time and poling temperature on the piezoelectric properties of PZT 45/55 films deposited by sol-gel technique was studied in order to optimize poling conditions. Short-term aging of d_{33} was also investigated to predict the piezoelectric behavior as a function of time. A poling field of 200 kV/cm and the poling time of 10-15 min was found to be sufficient for saturation of d_{33} and aging rate at room temperature. Further improvement of the piezoelectric properties was attained with an increase of the poling temperature until 150 °C. The piezoelectric coefficient was enhanced by 40-50% as compared to room temperature poling. The poling effect at elevated temperatures was found to correlate with the built-up of internal bias field which is responsible for the stabilization of domain structure after the poling field removal. The relevant activation energy was about 0.18 eV that may be related to the deep trap centers. Poling effect was compared for the films poled at 110 °C and cooled down under the poling field or under zero bias conditions. A poling under UV illumination was tried to improve the piezoelectric properties of PZT films. The mechanism of the poling effect on the piezoelectric properties of PZT films was proposed (compensation of depolarizing field by equilibrium and non equilibrium charge carriers).

4. Piezoelectric coefficient and strain were investigated in ferroelectric $SrBi_2Ta_2O_9$ (SBT) thin films. Though polarization and dielectric constant were small enough (5 $\mu C/cm^2$ and 180, respectively) the piezoelectric coefficients were sufficiently large reaching the value of 20 pm/V under the dc electric field. A strain of $6 \cdot 10^{-4}$ could be induced by the electric field of 300 kV/cm in these films. No piezoelectric fatigue was observed until 10^9 switching cycles in agreement with polarization data. Piezoelectric properties were succesfully described using a linearized electrostriction equation with the effective electrostriction coefficient significantly greater than for PZT family ferroelectrics. The electromechanical behaviour of BST films suggested no or weak contribution of non-180° domains to the piezoelectric response.

Collaboration with other institutions

1. ICMM CSIC, Madrid, Spain

Electromechanical properties of $Pb_{1-x}Ca_xTiO_3$ (PCT) films deposited at ICMM were investigated as a function of Ca content and processing conditions. Lead excess added to the solutions and rapid thermal annealing of the films were found to be essential to obtain good piezoelectric properties. Different Ca concentrations were tested to optimize piezoelectric response from the films. At x=0.24 the piezoelectric coefficient was about 70 pm/V that agrees well with the values previously reported for bulk ceramics. A giant strain (up to 1%) could be induced by the electric field in PCT films due to enhanced dielectric strength (>1 MV/cm).

2. "Jozef Stefan" Institute, Ljubljana, Slovenia

Piezoelectric and dielectric properties of PLZT and PZT films prepared at "Jozef Stefan" Institute were investigated in view of their possible applications as sensors and actuators. PLZT (8/65/35) thick films deposited by screen printing exhibited sufficiently strong piezoelectric activity under dc field. The d_{33} value was only two times smaller than in bulk ceramics of the same composition. The properties of the films were compared with the behavior of PLZT ceramics prepared from the same precursors. The results showed that very small grain size in the PLZT thick films and their high porosity can be responsible for their observed dielectric and piezoelectric properties.

Dr. B.Malic from "Jozef Stefan" Institute has been working as a post-doc for a half a year at EPFL on the processing and characterization of PLZT thin films. Different La precursors and processing conditions were tried to improve ferroelectric properties and endurance to fatique. The results showed that some imrovement of fatigue endurance can be achieved in La-doped PZT films.

3. RWTH, Aachen, Germany

Effect of ferroelectric polarization on the transient current response was investigated in PZT thin films prepared at EPFL and at RWTH. The work was done at RWTH as diploma thesis of S.Manetta (EPFL). The behavior of the relaxation current was described in the framework of phenomenological theory developed at EPFL.

4. University of Sheffield, Sheffield, England

The work was done during a short mission of Dr. I. Reaney at EPFL. Several TEM and EDS investigations of PZT and $PbTiO_3$ films were performed to examine the microstructure and compostion of the films near the bottom electrode interface. In thick multilayered films a Pb back diffusion was found to be far greater than in equivalent single layers. This was attributed to the greater thermal budget and stress that thick films have received. The TEM studies of fatigued films revealed their delamination at the interfaces not present in non-fatigued films. Further study is underway to confirm the relation between fatigue and delamination.

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4. D.V.Taylor, K.G.Brooks, A.L.Kholkin, D.Damjanovic, and N.Setter "Thickness dependence of electrical and electromechanical properties of sol-gel derived PZT thin films", Proc. of the Int. Conf. on Electroceramics, Aug.1996, Portugal (in press).
5. D.Damjanovic, D.Taylor, A.Kholkin, and N.Setter "Domain wall contributions to the piezoelectric properties of ferroelectric ceramics and thin films and their significance in sensor and actuator applications, Mat.Res.Soc.Symp.Proc. (in press).
6. P.Muralt "Piezoelectric thin films for MEMS", Int. Ferroelectrics (submitted).

COST 514: Reliability of Ferroelectric Thin Films

Institut für Werkstoffe der Elektrotechnik II
RWTH Aachen University of Technology

Yearly Report 1996

The Effect of Ferroelectric Polarization on the Transient Current Response of PZT Thin Films

M. Schumacher[1], S. Manetta[2], and R. Waser[1]
[1] Institut für Werkstoffe der Elektrotechnik (IWE)
RWTH Aachen University of Technology
D-52056 Aachen, Feral Republic of Germany[2] Laboratoire de Céramique
Ecole Polytechnique Fédérale de Lausanne
1015-Lausanne, Switzerland

Introduction

Continuing Tagantsev's work [1], we investigated the effect of ferroelectric polarization on the transient current response in PZT thin films in the short time regime.
The relaxation currents decreasing from 10^{-1} to 10^{-8} A/cm^2 were detected between 1µs and 1 second. The application of a varying poling field preceeded each measurement. The film was short-circuited in-between. Currents after given measuring times were plotted as functions of the poling fields: the I-P plots.

Results

Corresponding to [1], we observed that the relaxation current flowing against the polarization is always higher than the current flowing parallel to it. The irreversible ferroelectric contribution to the transient relaxation current obeys a Curie-von-Schweidlerlaw with a time exponent $m = 0.78$ in our case. This is in agreement with the domain wall creeping model proposed in [1] which is a good model to explain the irreversible ferroelectric contribution to the transient current.
Experiments show an increase of the current at a given time for increasing absolute values of the prepoling fields up to the range of the coercive field. The authors called this observed behaviour "seagull effect", which was observed to be stronger for Pt top electrode dots. The current decreases for increasing absolute values of the prepoling field higher than the coercive field. This was called "the bell phenomena". It was found to be relatively stronger for the additional investigated Au top electrode dots [2].

The experiments shows that the transient current is proportional to the reversible capacitance, even with respect to the seagull effect and the bell phenomena. This behaviour corresponds to the equivalent electrical circuit proposed in [1].

What is to better understood in the near future, is why and how the reversible polarization processes depend on the ferroelectric polarization. A direct correlation between the state of polarization and the absolute value of the relaxation losses is part of future investigations.

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Dielectric Properties, Leakage Behaviour, and Resistance Degradation of Thin Films of the Solid Solution Series $Ba(Ti_{1-y}Zr_y)O_3$

Susanne Hoffmann and Rainer Waser
Institut für Werkstoffe der Elektrotechnik II (IWE)
RWTH Aachen University of Technology
52056 Aachen, Federal Republic of Germany

Abstract

Barium titanate zirconate thin films were grown on Pt–coated Si–substrates by a chemical solution deposition (CSD) method at temperatures of 750°C. The crystal structure and the morphology of these films with respect to the Ti/Zr ratio were studied by means of glancing incidence X–ray diffraction analysis, scanning and transmission electron microscopy. The dielectric properties were analyzed as a function of the composition and the applied electric field. Using transient impedance analysis, the dielectric relaxation, leakage, and resistance degradation of the thin films were investigated with respect to the Ti/Zr ratio. The measurements show that thin films of the composition $Ba(Ti_{0.7}Zr_{0.3})O_3$ exhibit an improved DRAM charge storage behaviour compared to the pure $BaTiO_3$ films.

Introduction

Dielectric perovskite thin films of $Ba_{0.7}Sr_{0.3}TiO_3$ are widely investigated for thin film integrated capacitors and storage capacitors in DRAM applications[1][2]. The Sr substitution of Ba in $BaTiO_3$ shifts the ferroelectric to paraelectric phase transition towards lower temperatures[3]. Thus, the temperature dependent permittivity of conventional $Ba_{0.7}Sr_{0.3}TiO_3$ bulk ceramic exhibits a sharp maximum at room temperature. Although $(Ba,Sr)TiO_3$ thin films reveal a superparaelectric instead of a ferroelectric behaviour below the Curie–point, a shift of the maximum in permittivity to lower temperatures can still be observed. The high permittivity value combined with low dielectric losses due to the superparaelectric properties makes $(Ba, Sr)TiO_3$ one of the preferred candidates for DRAM applications. Besides a high permittivity, decisive factors in DRAM operation are a fast dielectric response, low leakage currents, and a long lifetime under dc voltage stress. In alkaline earth titanate bulk ceramics, the dominant mechanism causing resistance degradation is the motion of oxygen vacancies to the cathode of the capacitor, giving rise to induced enhancement of the electronic carrier concentrations which increases the conductivity and limits the lifetime of the capacitor.

The solid solution of $BaTiO_3$ and $BaZrO_3$ shows a lot of analogies to $(Ba,Sr)TiO_3$ solid solution. Firstly, in the $Ba(Ti,Zr)O_3$ system the tetragonal to cubic phase transition temperature can be shifted to lower values by increasing the Zr–content[4]. Secondly, investigations on ceramics have shown that in comparison to alkaline earth titanates the zirconates are more stable with respect to temperature and degradation. Therefore, $Ba(Ti,Zr)O_3$ ceramics a widely used as base material in ceramic multilayer capacitors (CMCs).

In the present paper, we present a comprehensive study on $Ba(Ti,Zr)O_3$ thin films which were deposited by the chemical solution deposition (CSD) method at temperatures of 750°C. Based on the data known from Ba(Ti,Zr)O_3 ceramics, we investigated Ba($Ti_{1-y}Zr_y$)O_3 thin films with compositions of $y = 0.0$ to 0.3 with respect to their electrical properties relevant for DRAM applications. Beside the composition, temperature, and voltage dependence of the relative permittivity, these are the short time relaxation behaviour as well as the leakage currents and the resistance degradation under dc voltage stimulation.

Results

As an alternative to the wide-spread consideration of BST thin films as high-permittivity dielectrics for future high-density DRAM devices, films of the Ba(Ti,Zr)O_3 solid solution series have been investigated. For a first comparative study of the influence of Ti being replaced by Zr, a chemical solution deposition technique is employed. From our results [5] we conclude the following:

1. Within the Ba($Ti_{1-y}Zr_y$)O_3 composition range of $y = 0 \dots 0.3$, single phase perovskite [6][7] films were obtained using a processing temperature of 700 to 750 °C.
2. All films exhibit a dense polycrystalline microstructure. The grain size decreases with increasing Zr-content up to $y = 0.25$, while films with $y = 0.3$ show a columnar microstructure.
3. The permittivity moderately decreases with increasing Zr-content. Presumably up to $y = 0.2$ this is due to the grain size reduction [8]. For potential DRAM applications, this is partly compensated by a reduction in the tunability of Zr-rich films.
4. The capability of maintaining the stored charge up to the next refresh cycle is improved with increasing Zr-content. This improvement can be related to a reduction of the relaxation and the leakage currents [9].
5. The relaxation currents exhibit a Curie-von Schweidler type time dependence [11] with a decreasing magnitude for higher Zr-content.
6. The onset of the field-enhancement of the leakage current [10] is shifted to higher field values for increasing Zr-contents. This leads to a very pronounced suppression of the leakage currents for high Zr-contents at large electrical fields.
7. The life time determined by the resistance degradation [12] of the film is considerably improved for increasing Zr-content.

In total, Ba(Ti,Zr)O_3 turned out to be potentially a better candidate as a high permittivity dielectric for future high-density DRAMs than the widely studied (Ba,Sr)TiO_3.

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ANNUAL REPORT 1996

RELIABILITY OF FERROELECTRIC THIN FILMS

Contribution:

Sol-Gel Processing of Thin Films with Ferroelectric or Conducting Properties

of the
COST 514 EU Concerted Action
"Ferroelectric Thin Films"

Institution: "Jožef Stefan" Institute, Ljubljana, Slovenia

Authors: M. Kosec, B. Malič, M. Mandeljc, G. Dražič

Ljubljana, May 1997

Objective: Chemical solution deposition (CSD) studies of PZT based thin films using various precursors (solution chemistry, pyrolysis, crystallization and microstructure)

Topics:

1. Influence of various Zr and Ti alkoxsides on the crystallization and microstructure of PZT based thin films prepared by the methoxyethanol route
2. PLZT thin film synthesis by the acetic acid route using $La(OAc)_3$ or $La(NO_3)_3$ hydrate and a varying excess of PbO.

Results:

1. $PbTiO_3$ (PT), $PbZrO_3$ (PZ) and PZT 53/47 films were prepared by the metoxyethanol route starting from transition metal propoxides or butoxides. Alkoxides of Zr and Ti were first reacted with $Pb(OAc)_2$ in their parent alcohols. The esterification reaction was followed by GLC. It was found that 90 % of the acetate groups were released in the butoxide system as compared to only 65 % released acetate group in the propoxide system, showing a predominant esterification reaction in the butoxide system and a significant acetate-alkoxide bridging reaction in the propoxide system.
   After the alkoxide-acetate reaction methoxyethanol was added and films were processed identically by the standard procedure.

   It was found that the alkoxide-acetate reaction has only a minor effect on the microstructure of PT and PZT films. However, the type of alkoxide strongly influences the microstructure of PZ films. A propoxide precursor solution results in a fine microstructure of less than 1µm grains, whereas a butoxide precursor solution yields a microstructure of several µm grain size.

2. Lead lanthanum zirconate titanate (PLZT) thin films with a Zr/Ti ratio of 65/35 and 4, 8 and 10 at % of La were prepared by the acetic acid based sol-gel route. Lanthanum was introduced into the starting solution as the acetate or the nitrate. A correlation between thermal decomposition, crystallization, microstructure and the use of different lanthanum precursors was observed. The PbO excess in the inner and the top PLZT layers was varied in order to get a pyrochlore-free microstructure.
   Upon pyrolysis La-acetate derived PLZT films contains a PbPt phase in addition to an amorphous phase, indicating strong reductive conditions during thermal decomposition of organics. A cluster-type microstructure in the randomly oriented perovskite phase is obtained upon RTA at 650°C.

   La-nitrate derived films pyrolysed without the appearance of PbPt phase. RTA films consist of a (111) oriented perovskite phase with 100nm grains.

   TEM analysis of La-nitrate based PLZT 4/65/35 films revealed that the perovskite grains possess a columnar structure and a population of nanometer-sized pores, probably formed as a result of PbO evaporation. Decreasing the PbO excess diminishes the pore population but also promotes surface pyrochlore formation.

Publications:

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Cooperation:

- Post-doctoral fellowship. Dr. Barbara Malič, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique: 15.1. - 15.7.1996 Topic: Processing and characterization of PLZT Thin Films.
- Short Term Sci. Mission, Dr. Barbara Malič, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, 18. - 29.11.1996, Research on PLZT thin films
- Visit, Dr. Marija Kosec, École Polytechnique Fédérale de Lausanne, Laboratoire de Céramique, 23.11.1996.
- Visit, Dr. Marija Kosec, Institut für Werkstoffe der Electrotechnik RWTH Aachen, 7.-8.11.1996.

- Cooperation within Copernicus ERB CIPA CT 940 236 Ferroelectric multilayer structure and thin films for actuator and microactuator applications. Partners: Ferroperm A/S Kvistgård, Denmark, Department of Ferroelectric Materials CSIC Madrid, Spain, Institut of Solid State Physics, University of Latvia, Latvia

COST 514: Reliability of Ferroelectrics Thin Films
Activities Yearly Report 1996

Ian M. Reaney

**Department of Engineering Materials, University of Sheffield,
Sir Robert Hadfield Building, Mappin St. Sheffield, S1 3JD,
England**

A large number of samples were investigated using TEM in order to determine the microstructure of films deposited by several differnt techniques.

Sputtered Films.

A study was made of $PbTiO_3$ films deposited onto both RuO_2 and Pt using virtually identical conditions in order to determine whether RuO_2 is a superior barrier to the back diffusion of Pb than Pt. Examination of the two samples using energy dispersive x-ray analysis (EDS) revealed that at the SiO_2/Pt interface Pb could be detected at all times and a mottling of the contrast just below this interface in the SiO_2 layer was considered to arise from the incorporation of PbO into the SiO_2 glass. In contrast, Pb was not detected at any time at the RuO_2/SiO_2 interface. Both of the samples were prepared by using a TiO_2 seed layer on the surface of the electrode prior to the deposition of $PbTiO_3$. In the Pt electroded sample, no evidence for the presence of this layer could be observed at the Pt/film interface and only porous $PbTiO_3$ could be observed. However, in the RuO_2 film, a dense layer of $PbTiO_3$ was observed immediately at the film/RuO2 interface upon which was a highly porous layer. It was concluded that the $PbTiO_3$ layer at the RuO_2/film interface arose from an in-diffusion of PbO into the TiO_2 while the outer porous layer nucleated separately on its surface.

Sol-gel films (comparison of multi and single layer films)

Comparison of the microstructure of 200nm and 1.5μm films were made in order to determine the effect of multilayering on electrode stability. A single layer 200nm film was examined with particular attention being paid to the electrode stability. Although, back diffusion of Pb into the SiO_2 could be observed to a small extent in this sample, in general it was not sufficient to cause potential adhesion problems and had primarily been arested at the Ti/TiO2 layer. A sample made using an identical deposition technique on the same type of substrate but 1.5μm thick was also investigated. The back difffusion of Pb was oberved all along the Pt/SiO2 interface in this case and a Pb-rich glass had formed. It was concluded that al though the electrodes were stable enough to produce thin films on the samples, they were still not good enough to support thick films deposited using a multilayering technique. It was considered that the back-diffused Pb might cause adhesion problems during piezoelectric measurements.

Examination of Fatigued Sol-gel Films

Thin sol-gel films were investigated in the fatigued and unfatigued state to determine the effect of these measurements on the film microstructure. Examination of the films revealed that all interfaces were delaminated in the case of the fatigued films while for the non-fatigued films the interfaces remained largely intact. This experiment was difficult to perform since it required the fabrication of an ion-beam thinned sample at a given fatigued electrode. Although the observation of delaminated interfaces is interesting, it is felt that further experiments are necessary to confirm that this is a reproducible feature in the mechanism of fatigue.

Summary

1) Pb diffusion could arrested using RuO2 electrodes but was ubiquitous with Pt

2) Thick multilayered films showed back diffusion far greater than equivalent single layer films. This is attributed to the greater thermal budget and stress that the have received.

3) Fatigue films were examined which suggested that there is an inherent weakness at the film interfaces not present in non-fatigued films. Further work is needed to confirm this.

COST 514

Report on the 1996 Yearly Activities of the Group Project:

Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

D.Wouters, April 1997

participants: IMEC (BE), VITO (B), MASPEC (IT), Univ. di Pisa (IT), EPFL (CH)

In spite of the lack of national funding for IMEC and VITO, and ending of the funding for AMSPEC, efforts were done to continue the research based on internal institute funding.

The research was focussed on the next 2 topics:

- RuOx for electrode and conducting barrier
- non-Pb containing ferroelectric films: LiTaO

Next results were obtained:
(more details can be found in the individual reports in addendum)

IMEC:

- deposition of RuOx by reactive sputtering
- influence of thermal treatments of RuO2
- RuO2/PZT/RuO2(/Pt) FECAP hysteresis and fatigue properties
- (PZT by sol-gel deposition)

VITO:

- deposition of RuOx by reactive sputtering
- samples -> MASPEC
  -> IMEC

MASPEC:

- PZT by sol-gel
- PZT/RuO2 capacitors

Univ. di Pisa / Messina:

- RuO2 by Pulsed Laser Deposition
- PZT/RuO2 and PZT/YBCO heterostructures

EPFL

- LiTaO3 by rf. sputtering

COST 514

ADDENDUM to
Report on the 1996 Yearly Activities of the Group Project:

Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

Yearly Reports of the individual participants:

- IMEC
- MASPEC
- Univ. di Pisa in cooperation with Univ. di Messina
- IPA-EPFL

COST 514: Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

IMEC Activities Yearly Report
D.Wouters, April 1997

Study of the sputter-deposition of RuO_2 electrodes

An extensive investigation of reactive sputtering of RuO2 was carried out. Films were deposited in different Ar/O2 mixtures, and different post-deposition thermal annealing conditions applied. The Ru/O content was investigated by RBS and XPS, in comparison with bulk RuO2 ceramic composition.
FECAPs with RuO2/PZT/RuO2/Pt/Ti/SiO2/Si structure with excellent hysteresis characteristics were obtained.

Study of the orientation control in multi-layer electroded structures

For PZT ferroelectric capacitors, the control of the orientation of the PZT is of primary importance in order to achieve good ferroelctric properties. For the displaced cell structure, Pt/Ti/SiO/Si can be used where the Pt deposited on Ti has an intrinsic "template" property, as it has a strong tendency towards (111) orientation. The PZT deposited by sol-gel deposition will crystallize hetero-epitaxially on this Pt, resulting in the advantageous (111) orientation of the PZT.

For the stacked capacitor cell, with a vertical bottom electrode contact, other contact materials and/or combinations have to be used, as RuO_2 or LSCO, eventually still in combination with Pt.

The orientration of both RuO2 and LSCO was investigated. It was observed that the RuO2 did not always follow the Pt orientation in a RuO2/Pt/Ti/SiO2/Si structure. Also LSCO (deposited by PLD) did not follow the Pt (111) orientation. On MgO susbtrates, LSCO followed MgO (100) orientation but not the MgO (111) orientation. LSCO (111) irientation could only be obtained on PZT (111).

COST 514:
Materials for a Ferroelectric Capacitor Stack with Direct Contact to Silicon

Yearly activities report MASPEC
B.Watts, April 1997

- Preparation of PZT on Ru and Ru/Ti, presented & published in the Proceeedings of the MRS Spring meeting.

- TEM work carried out in collaboration with Ancona:
  Pisa prepared RuO_2/PZT stacks on silicon showed that pyrochlore has a tendency to grow but a 5 min. anneal in 5-15mbar of O_2 at 700°C results in complete transformation to perovskite.
  Unfortunately, rough electrode prevented meaningful measurements of dielectric hysteresis.

- TEM measurements made on sol-gel samples. Paper published in Microelectronic Engineering

- The funding of the project ended. The last amount of funding was used to set up evaporation and sputtering equipment in the clean room in the Engineering Dept.

COST514 Action

Materials for a ferroelectric capacitor stack with direct contact to silicon

Annual report 1996

Maria Allegrini[1,2], Ennio Arimondo[1], Francesco Fuso[1],
Alfredo Iembo[1], Lidia Ceresara[1], Federico Cervelli[1],
Guglielmo Mondio[2], Fortunato Neri[2], Giuliana M. Currò[2], Giuseppina Montarro[2]

[1] *Istituto Nazionale Fisica della Materia, Dipartimento di Fisica,*
Università di Pisa Piazza Torricelli 2, I-56126 Pisa, Italy
tel. +39 50 911 285, 244; fax +39 50 48 277; e-mail: allegrin@ipifidpt.difi.unipi.it

[2] *Dipartimento di Fisica della Materia e Tecnologie Fisiche Avanzate,*
Università di Messina, Salita Sperone 31, I-98166 Sant'Agata, Messina, Italy

Scientific Report

The main aim of the group activity within the COST514 action is the fabrication of a ferroelectric stack on silicon-based substrates by pulsed laser ablation and deposition (PLAD). Thanks to its peculiarities (strong laser-target interaction, large kinetic energy of the vaporized material, easy control of the process parameters and applicability to different targets) this technique is very promising for completely in-situ fabrication of multilayers, especially for those composed of ceramic materials.

In our stacks we have used PZT ($PbZr_{0.52}Ti_{0.48}O_3$) as the ferroelectric material, and we have exploited RuO_2 conductive oxide, deposited on p-doped Si or Si/SiO_2, as the bottom electrode. In the last year, depositions have been carried out at Pisa exploring several choices of the process parameters, and the samples have been analyzed by SEM and X-ray diffraction, both in standard Bragg-Brentano method and in Grazing Incident Angle Bragg Diffraction (GIABD), which enables an investigation of top and bottom layer, as well as of the interface between layers. The results demonstrated the attainment of correct lattice structures, with a negligible contribution from pyrochlore PZT-phase. Electrical investigations (Sawyer-Tower method), performed by depositing Au dots as top electrodes, showed instead a poor interlayer insulation, which prevented any measurements of the ferroelectric hysteresis loop.

Such an unexpected behavior can be attributed to the relatively bad morphology of the RuO_2 layer, revealed by electron microscopy. Surface droplets and other splashing phenomena, enhanced by the use of a low density target (a cold pressed pellet made of 99.9% RuO_2 powder), can lead to the occurrence of cracks and creeps in the PZT layer, inducing shortening between electrodes.

However, also the stoichiometry of the RuO_2 layer could be responsible for the low resistivity of the PZT layer, through, for instance, an excess of surface Ru metal and subsequent diffusion across PZT. In order to definitely assess the stoichiometric quality of the RuO_2 films, samples have been deposited on Si or SiO_2 and a detailed analysis of the surface properties have been carried out at Messina through X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS). XPS investigations on the Ru 3d and 3p core lines revealed the presence of the correct RuO_2 stoichiometry, with a spin orbit splitting in excellent agreement with literature data on single crystals. Minor contributions ($\leq$ 10%) from a higher oxided species, ascribed to RuO_3, could be identified. Also EELS observations, which allowed us to measure for the first time the complex dielectric constant of laser ablated RuO_2 films in the range 0–40 eV, gave encouraging results, in close agreement with those reported in the literature for single crystals.

In addition, in order to check our multilayer deposition procedure, we carried out PLAD of YBCO/PZT bilayers on MgO and $TiSrO_3$, exploiting our experience, acquired in previous works, in the deposition of high temperature ceramic superconductors. Thanks to the use of a high density commercial $YBa_2Cu_3O_7$ target, it was possible to obtain a rather smooth surface in the bottom layer, as confirmed by atomic force microscopy (AFM) investigations. X-ray diffraction revealed the attainment of the correct structure for both YBCO and PZT layers. Polarization vs applied electric field measurements, performed by depositing Au test dots as top electrodes, displayed the presence of a good ferroelectric hysteresis ($P_r \geq 20\ \mu C/cm^2$, $E_c = 100$ kV/cm). These results confirm the capability of our set-up in fabricating multilayer structures and suggest indirectly that the poor electric behavior of RuO_2/PZT samples is related to the mediocre quality of the RuO_2 layer surface.

Future work

The future directions of our activity will be oriented toward the improvement of the RuO_2 layer surface through the use of a higher density target, made of metal Ru, which is expected to reduce the presence of creeps, and the search of suitable laser ablation parameters for inducing the formation of ruthenium oxide during the expansion of the ablated material (reactive PLAD). In addition, the interposition of interdiffusion barriers (Pt or Ti) between RuO_2 and PZT layers will be investigated. Samples produced with different choices of the process parameters will be analyzed through XRD, XPS and EELS.

Available facilities

At Pisa, the set-up for PLAD is based on a XeCl excimer laser (LambdaPhysik EMG101MSC - $\lambda = 308$ nm, $\tau = 16$ ns, $E_{max} = 150$ mJ) and two stainless steel deposition chambers, one equipped with in-situ process diagnostics facilities, the other with a multitarget holder for sequential multilayer deposition.
At Messina, a VG ESCALAB system is available. XPS analysis is performed using a VG scientific spectrometer, equipped with a standard twin-anode Mg/Al X-ray source and a 105° concentric hemispherical analyzer. EELS measurements are carried out under excitation from a VG LEG61 electron gun, operating typically at 1 keV, 10 μA emission current.

Collaborations with other COST514 groups

The fruitful cooperation with the group of MASPEC/CNR, Parma, Italy, already established in the last years, has continued with the preparation of PZT targets of different compositions and electrical characterization of ferroelectric layers (deposition and lithography for Au test dots, Sawyer-Tower measurements). In addition, a collaboration with Dipartimento di Scienze dei Materiali, Università di Ancona, Ancona, Italy, has made possible GIABD analysis of our RuO_2/PZT samples deposited on Si-based substrates. Finally, electrical investigation as a function of temperature and TEM observations of RuO_2 thin films have been carried out at Dipartimento Ingegneria dell'Informazione, Università di Pisa, Pisa, Italy.

Related publications

- PLAD of PZT on Si-based substrates:
  1. A. Iembo, F. Fuso, M. Allegrini, E. Arimondo, V. Berardi, N. Spinelli, F. Leccabue, B. E. Watts, G. Franco and G. Chiorboli, "*In-situ diagnostics of pulsed laser deposition of ferroelectric* $Pb(Ti_{0.48}Zr_{0.52})O_3$ *on Si*", Appl. Phys. Lett. **63**, 1194 (1993)
  2. M. Labardi, M. Allegrini, F. Fuso, F. Leccabue, B. E. Watts, C. Ascoli and C. Frediani, "*Scanning and Friction Force Microscopy (SFFM) of ferroelectric* $Pb(Zr,Ti)O_3$ *thin films*", Integr. Ferroelectr. **8**, 143 (1995)
  3. V.A.. Yakovlev, G. Mattei, A. Iembo, F. Fuso, E. Arimondo, M. Allegrini, F. Leccabue and B.E. Watts, "*Raman and Infrared Spectroscopy of Ferroelectric* $Pb(Zr_{0.48}Ti_{0.52})O_3$ *Films Deposited by Pulsed Laser Ablation*", J. Appl. Phys. **78**, 6321 (1995)

- PLAD of RuO_2 thin films on Si:
  4. A. Iembo, F. Fuso, E. Arimondo, C. Ciofi, G. Pennelli, G.M. Currò, F. Neri and M. Allegrini, "*Pulsed Laser Deposition and Characterization of Conductive* RuO_2 *Thin Films*", J. Mater. Res., in press (June 1997)
  5. G. Mondio, F. Neri, M. Allegrini, A. Iembo and F. Fuso, "*Energy Loss Spectroscopy of* RuO_2 *Thin Films*", J. Appl. Phys., submitted (1997)

- PLAD of PZT-based multilayers:
  6. L. Ceresara, A. Iembo, F. Fuso, M. Labardi, M. Allegrini, E. Arimondo, A. Diodati, B.E.Watts, F. Leccabue and G. Bocelli, "*Pulsed laser ablation deposition and characterization of superconductive/ferroelectric multilayers*", Supercond. Sci. Technol. **9**, 671 (1996)
  7. A. Iembo, F. Fuso, M. Allegrini, E. Arimondo, A. De Benedittis, A. Di Cristoforo, P. Mengucci, B.E. Watts and F. Leccabue, "*Preparation of* $Pb(TiZr)O_3/RuO_2$ *multilayers in situ by pulsed laser ablation deposition*", Integr. Ferroelectr., submitted (1997)

- In-situ diagnostics of the PLAD process for PZT:
  8. F. Fuso, L. N. Vyacheslavov, G. Masciarelli and E. Arimondo, "*Stark broadening diagnostics of the electron density in pulsed laser ablation of YBCO and PZT*"; J. Appl. Phys., **76**, 8088 (1994)
  9. S. Amoruso, V. Berardi, N. Spinelli, R. Velotta, M. Armenante, F. Fuso, M. Allegrini and E. Arimondo, "*Time-of-Flight Mass Spectrometry and Covariance Mapping Technique Investigation of Charged Species Evolution in* $Pb(Ti_{0.48}Zr_{0.52})O_3$ *Laser Ablation*", Appl. Surf. Sci. **86**, 35 (1995)
  10. S. Amoruso, V. Berardi, N. Spinelli, A. Dente, M. Armenante, R. Velotta, F. Fuso, M. Allegrini and E. Arimondo, "*Laser Ablation of* $Pb(Ti_{0.48}Zr_{0.52})O_3$ *Target: Characterization and Evolution of Charged Species*", J. Appl. Phys. **78**, 494 (1995)
  11. M. Allegrini, F. Fuso, G. Lorenzi, L.N. Vyacheslavov and E. Arimondo, "*Spectroscopy as in-situ diagnostics for pulsed laser deposition of superconductive and ferroelectric thin films*", Appl. Surf. Sci. **106** 438 (1996)

INSTITUT DE PHYSIQUE APPLIQUÉE

DÉPARTEMENT DE PHYSIQUE

PHB-Ecublens CH-1015 LAUSANNE Suisse
Téléphone: +41 (0)21 - 693 11 11
Téléfax: +41 (0)21 - 693 46 66 Télex: 454 478

ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

COST 514 : FERROELECTRIC CERAMIC THIN FILMS

Project:	Novel polarised ferroelectric thin films for silicon integrated devices
Applicant:	Prof. Francis Lévy Institut de Physique Appliquée Ecole Polytechnique Fédérale de Lausanne CH-1015 LAUSANNE (Switzerland)
Responsible scientist:	Dr. P.H. Schmid, IPA-EPFL
Coworkers:	C.H. Kohli X.X. Qu

PROGRESS REPORT FOR THE PERIOD 01.01.1996 - 31.12.1996

1. Summary of the work realized

1.1. *Thin film deposition and crystallisation*

Thin films of lithium tantalate are deposited at room temperature by r.f. sputtering from a commercial ceramic target, or by ion beam sputtering from a pressed powder target. The deposited films are amorphous and 100 to 600 nm thick. After thermal annealing, either standard or rapid at 600°C, the films are polycrystalline in the ferroelectric crystal phase.

1.2 *Characterisation*

The standard characterisation techniques include X-ray diffraction, secondary ion mass spectrometry, electron microscopies, local probe microscopies.

1.3 *Electrodes*

Two different electrode geometries were used in order to investigate the electrical properties of lithium tantalate thin films deposited on silicon substrates. In the first configuration, the properties of the films are measured between a bottom electrode and an upper electrode. The bottom electrode of ruthenium oxide is deposited before the deposition of the ferroelectric thin film. The top electrode (RuO_2 or Ni) is deposited after the thermal annealing of the film. For this geometry, electrical losses are observed especially if the film thickness is below 150 nm.

In the second configuration coplanar interdigited electrodes (RuO_2) are deposited either on tantalate thin film or directly on the oxidised silicon substrate before the tantalate deposition. Photolithographic and lift-off techniques are applied in order to realise the interdigited (20 µm) electrodes with an area of 2 mm^2 on the whole device size of 2 x 2 mm^2.

1.4 *Electrical measurements*

Electrical resistivity and permittivity are measured in the transverse configuration with an impedance analyser. The relative permittivity decreases with increasing frequency and increases with the thickness of the tantalate film. The resistivity decreases with the frequency as $\omega^{-0.7}$. At room temperature and 1kHz, the measured resistivity for a film thickness of 620 nm is $\rho = 2 \times 108$ Ωcm. The measured permittivity $\varepsilon_r = 40$ is comparable to the value measured on a lithium tantalate single crystal $\varepsilon_r = 25$. The permittivity as a function of the temperature increases and reveals the transition at the Curie temperature of 655°C.

The typical ferroelectric hysteresis is measured in a classical Sawyer-Tower circuit. At room temperature, the saturation polarisation is 24 $\mu C/cm^2$, the remanent polarisation 8 $\mu C/cm^2$ and the coercitive field 3kV/cm.

1.5 *Pyroelectric properties*

One of the main interests for the application of ferroelectric thin films relays on their pyroelectric response for infrared sensors. The pyroelectric structure (tantalate thin film + electrodes) is irradiated by a frequency modulated infra-red light beam. In the frequency range 0,6 Hz - 100 kHz, the pyroelectric response is measured with help of a lock-in amplifier. At room temperature and in the transverse configuration of the electrodes, the pyroelectric current normalised by the IR light power increases proportionally to the frequency up to 100 Hz. Above this frequency the value of 2.5 µA/W is stable up to about 1 kHz, where the normalised current reaches the value of 25 µA/W.

In the interdigited geometry, the pyroelectric current increases linearly with the frequency up to 2 kHz where it reaches the stabilised value of 400 µA/W, which is more than ten times larger than the value measured in the configuration with superposed electrodes. The pyroelectric coefficient calculated from the result in the interdigited geometry is 245 $\mu C/m^2K$.

The pyroelectric response can still be increased by a factor 3 after poling of the film in an electric field of 15 kV/cm during 5 s.

With increasing temperature, the pyroelectric response decreases. This behaviour is due to an additional resistivity of activation energy E = 0.43 eV. This parasitic resistivity is tentatively attributed to the surface contamination to electrical losses in the substrate or to electrical conduction in the grain boundaries.

The optimal thickness for the radiation/heat conversion in lithium tantalate thin films is of the order of 1µm since the absorption coefficient measured at wave length 15µm is 600 cm^{-1}.

2. Pyroelectric properties of $SbNbO_4$

Pyroelectric $SbNbO_4$ thin films were deposited on Pt coated silicon substrates by Ar^+ ion beam sputtering at room temperature. By rapid thermal annealing the films were crystallised after the deposition. Gold electrodes were deposited to build an experimental structure of the form $Au/SbNbO_4/Pt/TiO_x/SiO_2Si$. The pyroelectric response was analysed in the current and the voltage modes by two methods. The pyroelectric current is measured at low frequency (0,01 Hz) in standard furnace chamber, whereas the pyroelectric voltage is detected at 100 Hz under light irradiation, which is absorbed in the upper electrode of the device. The pyroelectric coefficient is found to be of the order of 50 $\mu C/m^2K$.

The investigation of this novel ferroelectric thin film reached an end in the present project since no obvious advantages were proven with respect to lithium tantalate.

3. Summary of the important results

- A new configuration of planar electrodes was tested on ferroelectric lithium tantalate thin films. They present significant improvements with respect to deposition and chemical reaction processes. They open new investigation possibilities of pyroelectric structures.
- Lithium tantalate thin films were demonstrated to be of acute interest for their stable pyroelectric properties with respect to largely investigated PZT ceramic thin films.

4. Collaborations

- Dr. D. Wouters	IMEC, Leuven/Belgium
- Dr. B. Watts	MASPEC-CNR, Parma/Italy
- Prof. N. Setter, Dr. P. Muralt	LC-DMX-EPFL, Lausanne/Switzerland

5. Meetings, seminars, conferences

- "Ferroelectric Thin Films" Workshop, COST 514 ICMM, CSIC, Madrid, 4-5.3.1996
  C.H. Kohli, P.E. Schmid, F. Lévy: "Electrical properties of lithium tantalate thin films on silicon substrates".

- Swiss Physical Society, Zurich, 10.10.1996
  C.H. Kohli, P.E. Schmid, F. Lévy: "Pyroelectrical properties of lithium tantalate thin film based devices with interdigital electrodes".

6. Financial report

Cf. Annex 1.

Microelectronics and Material Physics Laboratories
University of Oulu,
PL 444, FIN-90571 Oulu, Finland.

COST 514 Program Report of activities in 1996
Title of the project Pulsed laser ablation deposition of ferroelectric thin films
Project leader Prof. S. Leppävuori
Group members J. Levoska, T. Murtoniemi, M. Tyunina (visiting reseacher)

SUMMARY

Pulsed laser ablation deposition of lead-containning perovskites (mainly PZT related materials) and conducting oxide electrodes and their heterostructures by an *in situ* process has been studied, and the structure and properties of the films and heterostructures have been characterized.The latest studies have been concentrated on the deposition of LSCO electrodes and ferroelectric films on silicon using yttrium-stabilised zirconia buffer layers and on MgO. Studies of ambient gas pressure on the composition, thickness and surface morphology of PZT films in room temperature laser ablation process were carried out.

SCIENTIFIC RESULTS

In situ grown films

Layered thin film structures containing ferroelectric undoped, Nd doped or La doped lead zirconate titanate (PZT) and conducting lanthanum strontium cobalt oxide (LSCO) were deposited in an *in situ* process by pulsed laser ablation using an XeCl excimer laser and sintered polycrystalline targets. The structures were grown on heated MgO (100) single crystal substrates and on epitaxial laser ablated yttrium-stabilized zirconia (YSZ) buffer layers on Si (100) and silicon-on-sapphire (SOS).

The structure, orientation relationships and degree of epitaxy and crystal perfection of PZT films were studied by X-ray diffraction, scanning electron microscopy (SEM) and micro-Raman specroscopy. Good crystal perfection, phase purity and epitaxy of (110) oriented trigonal PZT was obtained on epitaxial LSCO electrodes deposited on MgO. On the films on YBCO/YSZ/Si (or SOS), both (100) and (110) oriented PZT was observed. It was found that almost purely (110) oriented PZT can be grown on LSCO/YSZ/Si under proper conditions.

Capacitor structures were were fabricated using masking during the deposition. Laser ablated Pt top electrodes were used. Ferroelectric properties of PZT films and resistive properties of the structures were measured both at room temperature and cryogenic temperatures. For the films on LSCO electrodes on MgO, the maximum polarization at an electric field of 220 kV/cm was 30 $\mu C/cm^2$, the remanent polarization 18 $\mu C/cm^2$ and the coercive field 62 kV/cm. For the films on Si and SOS with LSCO electrodes, the saturation polarization at an electric field of 400 kV/cm was about 55 $\mu C/cm^2$, the remanent polarization 36...37 $\mu C/cm^2$ and the coercive field 75...80 kV/cm.

Laser ablation process

Growth rate and composition of films deposited using laser ablation of $Pb(Zr_{0.65}Ti_{0.35})O_3$ both in vacuum and in ambient oxygen and argon, at laser fluence in range 0.3 ... 3.0 J/cm^2 were studied experimentally by energy dispersive x-ray analysis. The film growth rate increased in vacuum with increasing laser fluence, and demonstrated two modes of behavior upon adding gas: the growth rate decreased at low laser fluence and increased non-monotonously at high laser fluence. Deposition in vacuum resulted in Pb deficient films with Pb/Ti ratio decreasing with increase in laser fluence, while deposition in a gas resulted in a strong increase of Pb content with Pb/Ti ratio increasing faster under strong laser irradiation. The changes in film growth rate and composition were similar upon adding either oxygen or argon. No noticeable changes in the spatial distribution of the film growth rate and composition were found in a gas with respect to vacuum. The obtained experimental results were analyzed using a phenomenological description of the film growth as a sorption of ablated species on the substrate surface and assuming the species retarding in a gas, with respect to vacuum, due to collisions of the species with gas molecules.

The surface morphology of above-mentioned films was studied using scanning electron microscopy and atomic force microscopy. Film surface roughening depended on the pressure and nature of ambient gas, as well as on the duration of deposition. The development of surface features was discussed in terms of species adsorption and surface diffusion. The power law dependence of surface roughness on the number of laser pulses, observed in oxygen and in argon, can be explained assuming a non-thermal mobility of atoms on the surface with adatom-cluster barriers formed due to cluster generation in the plume.

PUBLICATIONS

J. Levoska, T. Murtoniemi, J. Lappalainen, S. Leppävuori, Deposition of epitaxial ferroelectric lead zirconate titanate and conducting oxide electrodes by pulsed laser ablation, Ferroelectrics 186 (1996) 207-210.

M. Tyunina, J. Levoska, S. Leppävuori, Experimental studies and modeling of PZT film growth in pulsed laser deposition, to be submitted to J. Appl. Phys..

M. Tyunina, J. Levoska, J. Koivusaari, S. Leppävuori, Surface morphology during pulsed laser deposition of $Pb(Zr,Ti)O_3$, to be submitted to Appl. Phys. Lett..

ANNUAL REPORT 1996

COST514 Action on "Ferroelectric Thin Films"

Group project: **Ferroelectric Thin Films for SAW devices**

Participants:

- Instituto de Ciencia de Materiales de Madrid, CSIC (Spain). Prof. J. Mendiola.
- Ferroperm A/S. Piezoelectric Ceramics Division, Hejreskovvej (Denmark). Ms. Wanda Wolny.
- Materials Science Center, Univ. of Manchester (UK). Dr. David Hall.
- CEMES-LOE/CNRS, Tolouse (France). Dr. Etienne Snoeck.

Objetives:

- Development of modified lead titanate thin films by laser ablation and sol-gel.
- Microstructural characterization of the films.
- Measurement and optimization of functional properties (piezo and pyroelectric)
- Preparation and test of SAW devices on the thin films.

A report of CSIC group is attached with details on the developed activities.

Activities in cooperation,

- Within the group:

- Short term scientific mission of Dr. P. Ramos (CSIC) at CEMES-LOE, Tolouse (France), to carry out the microstructural characterization of Ca-modified lead titanate films, under the supervision of Dr. Snoeck. The grain size distribution of the films was determined by TEM and the SAED patterns were obtained in $(Pb,Ca)TiO_3$ films obtained with different PbO excess content and thermal treatments.

- Within the COST514 Action:

- Short term scientific mission of Dr. R. Sirera (CSIC), visiting the Universities of Aveiro and Minho (Portugal) under the supervision of Dr. P. Mantas and Dra.M.J. Matos Gomes. The Raman spectra of $(Pb,Ca)TiO_3$ films was obtained.

- Cooperation with Dr. M.Kosec (JSI, Slovenia) and Ms. W. Wolny (Ferroperm A/S, Denmark) through the Copernicus project ERBCIPA-CT94-0236 on "Ferroelectric multilayer structures and thin filmsfor actuator and microactuator applications". Other partner: Dr. Sternberg (University of Latvia at Riga). Analysis of the precursor solutions for pure and Ca, Sm and La modified $PbTiO_3$ by TGA/EGA in oxigen and oxigen/argon mixture atmospheres was carried out.

- Sol-gel samples of Ca and La-modified lead titanate were sent by Dr. M.L. Calzada from CSIC (Spain) for piezoelectric coefficient measurement by Dr. A. Kholkin at EPFL (Switzerland).

Results obtained

- Deeper knowledge of the thermal decomposition of the precursor solutions of the pure and modified lead titanate thin films obtained by sol-gel, as well as of the microstructure of the films prepared under different thermal treatments.

- Development of thermal and electrical treatments (conditioning treatments) to enhance the ferroelectric performance of the thin films and understanding of the underlaying mechanisms causing this effect.

- Measurement of functional properties of the sol-gel thin films, pyro- and piezoelectric coefficients. Interesting results were obtained and deserve further exploration.

- New attempts to obtain SAW response in the films optimized during the previos period of development of the project were unsuccesfull due to problems in the IDT deposition and the limitations in the avaliable equipment for poling of the films.

Future trends

- Efforts to determine the SAW characteristics of the sol-gel samples will continue.

- Since the pyro- and piezoelectric characteristics already measured are very promissing , we expect to widen the scope of the present project through the collaborative work on these topics with other groups participating in the COST 514 Action or to be incorporated to it.

ANNUAL REPORT 1996

COST514 Action on "Ferroelectric Thin Films"

Group project: **Ferroelectric Thin Films for SAW devices**

Partner : **CSIC.** Responsible Scientist: Prof. J. Mendiola.

The main features of the research carried out during the last year concern the progress in the preparation of thin films of Ca and La modified lead titanate by sol-gel method [1]. Improvements of the ferroelectric performances have been obtained such as higher remanent polarization, reduced fatigue and larger piezoelectric [2] and pyroelectric activity.

The application of thermal treatments [3] to the samples Ca-modified films was found to be the most convenient technique to improve their ferroelectric behaviour when they are applied before the ferroelectric measurements. These effects are explained on the bases of the charged defects and strain developed during the processing [4]. A thesis was completed, among others, on this topic by P. Ramos, under the title "Study of the ferroelectricity of sol-gel thin films of Ca- modified lead titanate". TEM results obtained at CEMES-LOE (Toulouse, France) were included in this thesis.

Also in this period, a thesis on "Pulsed laser ablation deposited thin films" was completed by M.J. Martin. Ceramic targets of (Pb,Sm)TiO_3 prepared by Ferroperm, with adequate PbO excess, and provided to CSIC in the frame of the COST514 Action, were used in this thesis for the preparation of the corresponding films. For these an strong dependence of the ferroelectric properties was found on the degree of epitaxy with the substrate and the domain orientation of the as-deposited films.

Within a project in cooperation with Ferroperm, M. Algueró is developing a thesis work on the structure-properties relationships of La-modified thin films, which were interesting for their good piezoelectric properties, determined at EPFL by Dr. Kholkin, which made them usefull as microactuators[5]. These films have also potential interest to be used as SAW substrates and will be tested in the future.

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Summary of the Activities in the Year 1996

PREPARATION AND CHARACTERIZATION OF FERROELECTRIC THIN FILMS BY SOL-GEL PROCESSING

Macit ÖZENBAŞ

Department of Metallurgical and Materials Engineering
Middle East Technical University
Ankara, 06531 Turkey

The present work describes the preparation of Pb(Zr,Ti)O_3 thin films from metal chlorides by homogeneous precipitation using urea. The rate of decomposition of urea is very slow and the particles formed are very small in size (micron-sized) and highly homogeneous in composition. The coating of the films was carried out on alumina and Pt-coated silicon substrates in an ambient atmosphere. Heat treatment temperatures in excess of 800°C were required to ensure that the perovskite phase dominated in PZT films.

EXPERIMENTAL PROCEDURE

$PbCl_2$ (powder), $ZrCl_4$ (powder), $TiCl_2$ (aqueous) together with some urea are the starting materials for preparation of PZT thin films using homogeneous precipitation in the presence of additives as described below:

- Throughout the process stock solutions are used,
- Hydrochloric acid are used to regulate the pH of the solution (= 5.5),
- Additives poly styrene and methyl cellulose helps gel formation,
- Urea decreases precipitation rate and results in very fine particle size($< 1\mu m$).

Figure 1 shows the production route for the preparation of PZT films. The substrates used throughout this study were Si (111) wafers, Pt-coated Si (111) wafers and α-Al_2O_3 and dip coating was used as the coating method for PZT films because of being a cheap and easy method compared to other frequently used methods such as spin coating and others. The coating of the films were done just before precipitation takes place in the solution. The coated substrates were dried at 100-150^{0}C in ambient atmosphere. This process can be repeated in order to increase the thickness of the films.

To determine the complete crystallization temperature of the films, they were annealed at 350°C, 550°C, 650°C, 750°C, and 850°C. The last temperature was found to be the appropriate temperature which yielded complete perovskite phase.

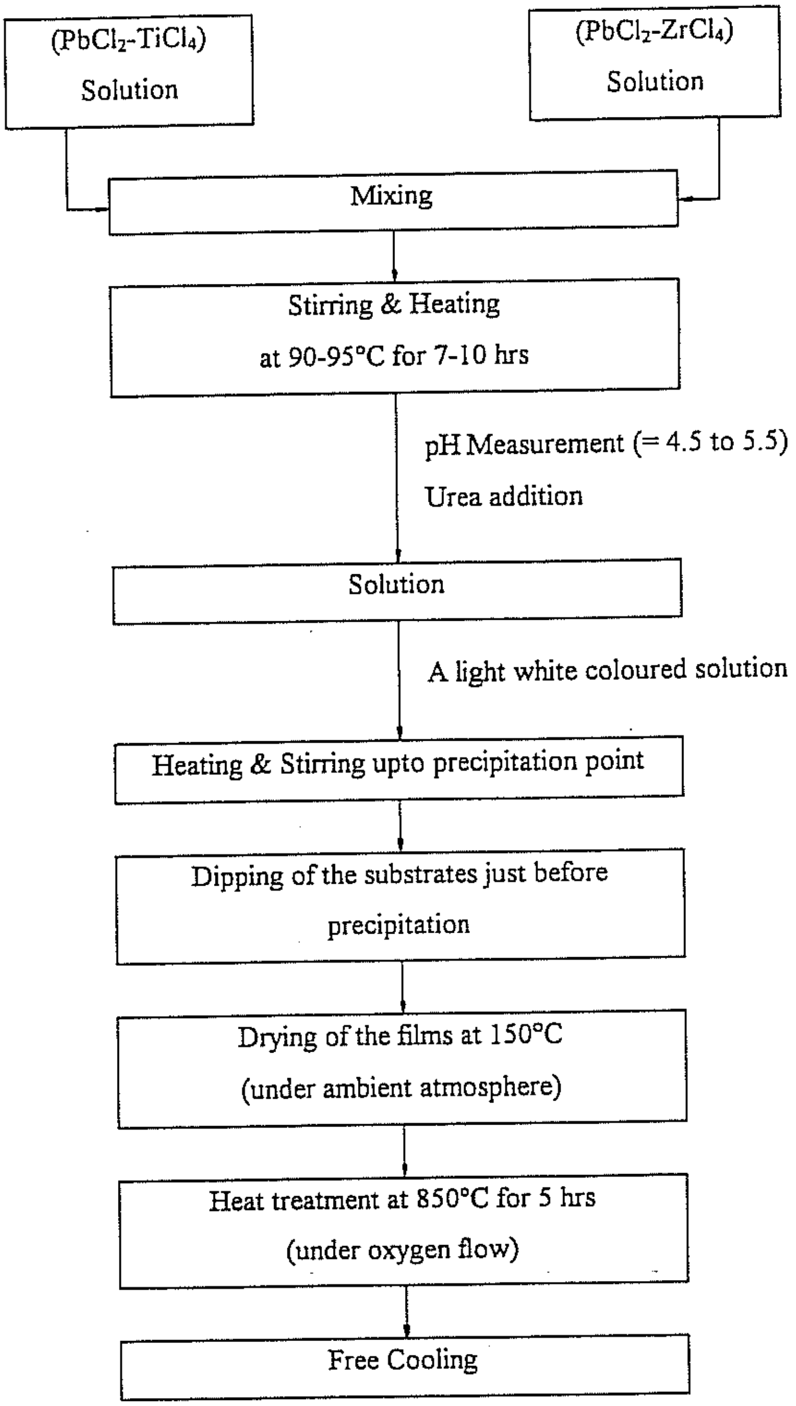

Figure 1. Production route for the preparation of PZT films.

RESULTS

PZT Powders

- The resulting PZT powders prepared with and without the addition of urea during processing have the desired stoichiometry but only the ones prepared with using urea had the desired particle size of submicron range.
- The powders were annealed at various temperature and time intervals. By this way, the phases transformed were predicted by using XRD diagrams. The following table shows the improvement obtained by successive heat treatment stages in the combined form. This table emphasizes the fact that 850°C-5 hours treatment combination is the optimum temperature and time factors to have the desired crystal structure.

Temperature (°C)	Time (hour)	Present Phases
550°C	5	$PbTiO_3$, Pyrochlore, Perovskite
750°C	5	Pyrochlore, Perovskite
850°C	3	Pyrochlore, Perovskite
850°C	5	Perovskite

- PZT powders obtained by sintering them at 850°C for 5 hours showed no chlorine residuals in the system as indicated by EDX analyses. The same result was also achieved by FT-IR spectra taken from the samples annealed at different temperatures.

PZT Films

- A series of experiments were performed in order to obtain films of different compositions and solution characteristics, and annealing temperatures were changed in every experiment to find most convenient composition, annealing temperature, wetting characteristics and thickness of the films.
- Wetting of the films are better on alumina and Pt-coated Si substrates compared to that on bare Si substrates. Wetting characteristics are dependent mainly on surface morphology of the substrates.
- The heat treatment operations of both the ferroelectric PZT powders and films were done under controlled O_2 atmosphere in a tube furnace. The oxygen flow rate was chosen to be 250ml/min for heating and they were left in the furnace from the sintering temperature down to room temperature under flowing oxygen. The samples were heat treated in alumina crucibles. The resulting crystal structure of sol-gel derived PZT films and powders were highly sensitive to both the initial composition, heat treatment temperature and time.
- As in PZT powders, similar annealing temperatures were also used to obtain PZT films starting from 350°C to 550°C, 750°C, and 850°C to obtain the perovskite structure. 850°C and 5 hours combination was found to be the optimum heat treatment temperature and time. The chlorine content of the initial dried film was decreased by increasing both the treatment temperature and time and, finally 850°C-5 hours sintering yielded no-chlorine in the film.

- X-ray mapping of PZT films on α-Al_2O_3 and Pt-coated Si substrates annealed at 850°C for 5 hours showed that PZT films were homogeneous in chemical composition.
- Due to smaller particle size achieved by using urea, the films obtained by using urea addition showed a decrease both in the film thickness and surface roughness (Figure 2). This figure also shows well adherence characteristics of the film to the substrate.

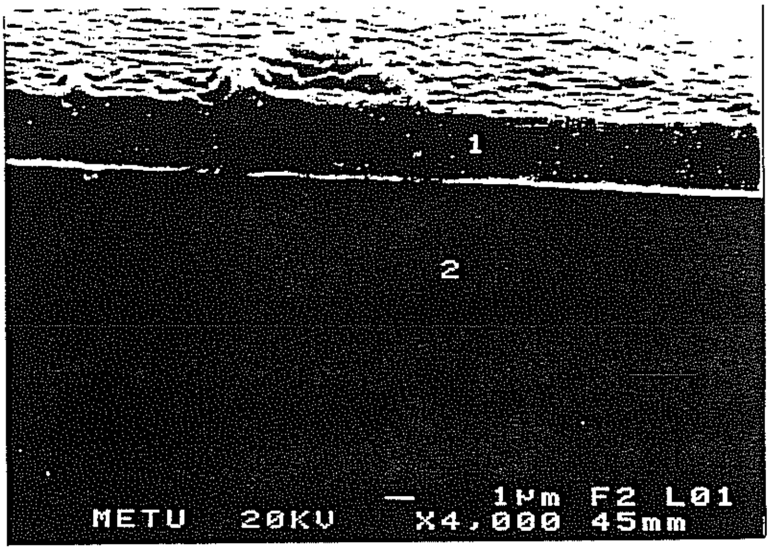

Figure 2. SEM micrograph of the PZT film on Pt-coated Si substrate heat treated at 850°C for 5 hours (prepared with the addition of urea).

Publications :

1. M. Özenbaş, "Preparation of PZT Films and Powders by the Sol-Gel Process", Workshop of the COST 514 - European Concerted Action on Ferroelectric Thin Films, March 4-5, 1996, ICMM.CSIC. Madrid, Spain, pp.43-46.

2. M. Özenbaş and Ü. Ergin, "Preparation of $Pb(Zr,Ti)O_3$ Thin Films and Powders by the Sol-Gel Process", Ferroelectrics, 1996, Vol. 186, pp. 219-222.

Financial Status :

A limited budget is available for chemicals and substrates till the end of 1997.

European Concerted Action on Ferroelectric Ceramic Thin Films COST 514
SUMMARY of the ACTIVITIES (from October 1995 to July 1996)

Group Project : *Optical and Non-Linear Optical Properties of Ceramic Thin Films*

1. Portuguese Participants

- Departamento de Física, Universidade do Minho, 4709 Braga, Portugal,
Scientist responsible: Dr.M.Jesus M. Gomes

- Departamento de Engenharia Cerâmica e do Vidro, Universidade de Aveiro, Aveiro, Portugal.
Scientist responsible: Dr.P.Mantas

This collaborative project includes research topics related to growth and study of ceramic thin films for electrical, optical and electro-optical applications.

2. Research Work Carried Out in the frame of the Project

2.1. Materials and Film Processing and Characterization

Pulsed laser ablation, magnetron rf-sputtering, ion-beam sputtering and sol-gel techniques has been used to grow the films.
Thin film processing of PZT, PLZT and lithium tantalate, $SbNbO_4$ have been carried out.Ceramic sintering technique has been used to prepare PLZT targets to be used in laser ablation.

2.2. Materials and Film Characterization

Structural and chemical characterization of the targets and deposited films has been made using the X-ray and EDX techniques.

The following optical properties of the targets and deposited films have been measured:

* Optical absorption (transparency in the near ultraviolet (NUV)-visible (V)-near infrared(NIR) range)
* Optical reflectance in the range NUV-V-NIR;
* the refractive index and absorption coefficient;
* Raman scattering;
* Infrared reflectance using FTIR optical spectroscopy.

3. Members Contribution - Summary of Progress

3.1. Departamento de Engenharia Cerâmica e do Vidro, Universidade de Aveiro

This group have prepared PLZT targets of the composition 9/65/35, and of several PbO excess contents ranging from 0.5 to 10%.

The targets have been used by the group of Minho, to grow the PLZT films mentioned below.

3.2. Departamento de Física, Universidade do Minho

a) PZT films have been grown onto a glass substrate using the magnetron rf-sputtering technique. The films were grown from a multi-element metal target in an oxygen/argon (O_2/Ar) reactive atmosphere. The target consists of alternately arranged titanium and zirconium targets (total sputtering area ratio of Zr/Ti is 1) and several Pb-pellets. Several sputtering conditions- O_2/Ar gas mixed rate, substrate temperature, and annealing conditions have been tried in order to study the growth of the perovskite phase.

b) Films of PLZT have been grown by pulsed laser ablation (Nd:YAG nanosecond laser, 1064 nm) using sintered powder targets prepared in Aveiro (Dept. Ceramic Engeneer and Glass) with several compositions, 8/65/35 and 9/65/35, onto glass substrates. Several deposition conditions- deposition temperature and deposition O_2 pressure, and annealing conditions have been studied in order to obtain a pure perovskite phase.

c) Films of PLZT have been grown by pulsed laser ablation. Commercial targets of the composition 9/65/35 are being used to grow PLZT films onto glass, $SrTiO_3$, and sapphire single-crystalline substrates. Some of the films have been prepared using the pulsed laser ablation system (excimer laser, 325 nm) at MASPEC Institute. Several deposition conditions like deposition temperature, O_2 pressure and laser power are being tried in order to obtain the perovskite phase.

d) Structural characterizations were carried out using X-ray diffraction. The chemical characterization of the PZT and PLZT films was performed using EDX analysis.

e) The optical characterization of the PZT and PLZT films includes: optical transmission, absorption band-gap, refractive index, Raman scattering and IR reflectance (FTIR-Raman) ;
Raman scattering and infrared (FTIR) spectroscopic measurements of the targets have been made and compared with those obtained from the films.

4. Publications

Some of the results obtained with PLZT films prepared in b) have been published:
M.J.M.Gomes, E.de Matos Gomes, P.L.Q.Mantas, J.L.Baptista, Applied Surface Science **96-98** (1996) pp. 779-783.

European Concerted Action on Ferroelectric Ceramic Thin Films COST 514

SUMMARY of the ACTIVITIES (from October 1995 to July 1996)

Group Project : *Optical and Non-Linear Optical Properties of Ceramic Thin Films*

Italian partners
Istituto MASPEC/CNR, Via Chiavari 18/A Parma
Centro CSSD/CNR, Viale delle Scienze, Parma
Dipartimento di Fisica, Università di Pisa, Pisa

The objective is to study optical properties of ceramic ferroelectric thin films and their possible applications. The techniques used to grow the films are sputtering, pulsed laser deposition and sol-gel.

The work which has been carried out in the last period can be summarised:

1. Pulsed laser deposition of PLZT on $SrTiO_3$ and MgO by sol-gel and pulsed laser deposition.

Films have been deposited by PLD on MgO and $SrTiO_3$ showing well oriented growth. These films are being analysed optically.
Oriented PZT has been grown on MgO by sol-gel. Grazing Incident Angle Bragg Diffraction shows that films grew (001) oriented from the solid phase. This effect seems to depend on the Zr:Ti ratio, since it is quite marked in a film of composition $PbZr_{0.25}Ti_{0.75}O_3$ but no oriented growth was seen in $PbZr_{0.52}Ti_{0.48}O_3$. Probably, the tendency to crystallised the pyrochlore phase is detrimental to this type of growth habit.

2. Study of $LiTaO_3$ deposited by sputtering.

Thin amorphous films of $LiTaO_3$ deposited on glass substrates by sputtering were recrystallised at different temperatures. Atomic force microscopy shows an aligned, polycrystalline morphology. The films will be studied using grazing angle XRD in order to determine the growth mechanisms.

3. Development of other collaborative projects

An ALFA programme (type B1) has been started and two group meetings have been organised the first during the EUROCERAMICS V Conference in Aveiro in September '96, and the second at the COST 514 Workshop on "Ceramic Ferroelectric Thin Films", held in Parma in April '97. The project is coordinated by the MASPEC/CNR group and also involves the University of Braga and NMRC, Cork. The current meetings are to set up a B3 type project will involve the exchange of postgraduate (Doctors and Masters) students. The environment of the COST Action is proving an ideal framework for its development.

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Acronyms - Comdocuments - Contacts

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BIBLIYOGRAFIK BILGI FORMU

1- Proje No: MİSAG/COST-514

2- Rapor Tarihi: Ağustos 1998

3- Projenin Başlangıç ve Bitiş Tarihleri: Şubat 1994 - Şubat 1998

4- Projenin Adı: Ferroelektrik Seramik İnce Filmler

5- Proje Yürütücüsü ve Yardımcı Araştırıcılar:
Prof. Dr. Macit Özenbaş
S. Ümit Ergin
Tufan Güngören
Nilgün Turhan

6- Projenin Yürütüldüğü Kuruluş ve Adresi:
Orta Doğu Teknik Üniversitesi
Metalurji ve Malzeme Müh. Bölümü

7- Destekleyen Kuruluş(ların) Adı ve Adresi: TÜBİTAK

8- Öz (Abstract):

Bu çalışmada ferroelektrik özellikli Pb(Zr,Ti)O_3 filmler ve tozlar sol-jel yöntemi kullanılarak elde edilmiştir. Tozlar sulu çözeltiden homojen çökeltme, filmler ise çökelme öncesi daldırma yöntemi kullanılarak üreli ortamda hazırlanmışlardır. Altlık malzemesi olarak platin kaplanmış Si-(111) dilimleri, Si dilimleri ve α-Al_2O_3 kullanılmıştır. Filmlerin ve tozların karakterizasyon işlemleri için öncelikle XRD ve SEM/EDS kullanılmıştır. Parça boyutu, morfolojisi ve film yüzeyleri SEM çalışmaları ile gözlemlenmiş, film ve toz bileşimleri EDS analizleri alınarak araştırılmıştır. Isıl işlem esnasında bir kaç kez XRD analizleri alınarak oluşan fazlar belirlenmiştir. Toz örneklerin içerdiği safsızlıkların belirlenebilmesi amacı ile spektroskopik IR analizleri yapılmıştır. 850°C'de, 5 saat boyunca ısıl işleme tabi tutulmuş bütün tozlar ve filmlerin perovskit faza geçerek tamamen kristalize olduğu ve stokiyometrik olduğu belirlenmiştir. 350°-650°C ısıl işlem sıcaklıkları arasında perovskit, piroklor, ve kurşun titanyum, 650-850°C arasında ise perovskit ve piroklor fazlar gözlemlenmiştir. Platin kaplanmış Si üzerinde üre kullanılarak elde edilen PZT filmlerin polarizasyon histeresis eğrisinden elde edilen artık polarizasyon (P_r) ve koersiv alan (E_c) değerleri, ~22 $\mu C/cm^2$ ve ~20 kV/cm, olarak belirlenmiştir. Aynı filmlerde dielektrik katsayısı ise 562 olarak hesaplanmıştır.

Anahtar Kelimeler: PZT, ferroelektrik filmler, sol-jel yöntemi.

9- Proje ile ilgili Yayın/Tebliğlerle ilgili Bilgiler

- M. Özenbaş, S. Ü. Ergin, "Preparation of Pb(Zr,Ti)O_3 Thin Films and Powders by the Sol-Gel Process", Ferroelectrics, 1996, Vol. 186, pp. 219-222.
- M. Özenbaş, "Sol-Gel Processing and Characterization of Ferroelectric Pb(Zr,Ti)O_3 Films and Powders", MRS Fall Meeting, 1-5 December 1997, Boston, USA, p.495.

10- Doçentlik B. Dalı Kodu: 604.02.00
Uzmanlık Alanı Kodu: 604.02.07
ISIC Kodu:

11- Dağıtım (*) : ☐ Sınırlı ☒ Sınırsız

12- Raporun Gizlilik Durumu : ☐ Gizli ☒ Gizli Değil

(*) Projenizin Sonuç Raporunun ulaştırılmasını istediğiniz kurum ve kuruluşları ayrıca belirtiniz

TÜBİTAK Yayın - Dağıtım Daire Başkanlığı 92 - 00