

SYMPOSIUM PM07

Plasma-Based Synthesis, Processing and Characterization of Novel Materials for Advanced Applications
November 26 - November 28, 2018

Symposium Organizers

Davide Mariotti, Ulster University
Tomohiro Nozaki, Tokyo Institute of Technology
Mohan Sankaran, Case Western Reserve University
Chi-Chin Wu, U.S. Army Research Laboratory

* Invited Paper

SESSION PM07.01: Carbon and Organic Materials
Session Chairs: Sumit Agarwal and Mariadriana Creatore
Monday Morning, November 26, 2018
Hynes, Level 1, Room 107

8:30 AM *PM07.01.01

Mass-Production of CNT Materials from Gas Phase Chemical Vapour Deposition and Microwave Plasma Brian Graves, Fiona Smail and Adam Boies; Engineering, University of Cambridge, Cambridge, United Kingdom.

The exceptional mechanical, thermal, and electrical performance of carbon nanotubes (CNTs) makes them ideal for a wide range of applications, however they are costly to produce and difficult to integrate effectively with other materials. We have developed several continuous gas phase CVD processes that can synthesize novel CNT bulk-produced materials at high mass-throughput.

The presentation will demonstrate how CNTs can be grown and synthesized into macroscopic materials using continuous gas phase processes. In a tube furnace, CNTs are grown with gas phase CVD from catalyst particles comprised of a transition metal and sulphur. As the CNTs increase in length and number concentration, they agglomerate to form an aerogel which can be extracted continuously from the reactor. The self-assembled CNT structure can be wound to form fibres and mats which can be easily integrated into composites, wires, and heat pipes, among many other applications. New developments of this process will be discussed along with the properties and applications of the resulting CNT materials.

We are also currently working towards replicating this aerogelation process with a microwave plasma reactor, in which we have previously synthesized a metal oxide – CNT composite material for the anodes of lithium ion batteries. This plasma-based process exhibits several key advantages over other techniques. The extremely high temperature of the plasma permits vaporization of a wide range of precursor materials, including those in powdered, elemental form which are ideal for an industrial process since they are cheap and readily available. The plasma also has a high energy density, meaning that a large mass throughput can be achieved with a small system. Large-scale production of these materials with this method could contribute to significant advances in materials for an array of engineering fields.

9:00 AM PM07.01.02

Plasma Activation of Carbon Fiber Reinforced Thermoplastics Trey Oldham¹, Daniel R. Ferriell², Marcus A. (Tony) Belcher², Alexander Rubin² and Elijah Thimsen¹; ¹Washington University in St. Louis, Saint Louis, Missouri, United States; ²The Boeing Company, St. Louis, Mississippi, United States.

Carbon fiber reinforced thermoplastic (CFRTP) composites are a platform material for structural applications due to their high fracture toughness, lightweight, and chemical resistance. However, the chemical inertness of the thermoplastic hinders the material's ability to robustly bond to form structural assemblies. Non-thermal plasma treatments of CFRTP composites have been shown to overcome this limitation by producing an activated surface. The highly reactive surface comprised of ions and radicals is intrinsically unstable, resulting in the deterioration of the activation state over time. The ability to characterize the activation state is of significant importance in terms of quality control of bonded structural assemblies. In this work, a novel, non-destructive method of determining the activation state of plasma-treated surfaces was discovered using Kelvin probe force microscopy (KPFM) surface potential measurements. Activated surfaces are characterized by a sharp, well-defined surface potential distribution. The sharp peak is hypothesized to be due to the presence of quasi-stable radical-ion complexes. Plasma-treated CFRTP surfaces being uniformly comprised of anionic and radicalic species is supported by KPFM, contact angle, magnetic force microscopy (MFM), and radical scavenger experiments. Radical-anion complexes are only stabilized when both species are present (i.e. radicals readily react in the absence of anions and vice versa). Evidence in support of radical-anion stabilized complexes was observed by a decrease in radical scavenging activity of a plasma-treated sample which had been charge-neutralized compared to non-neutralized plasma-treated sample. MFM measurements provide an independent verification of this result.

9:15 AM OPEN DISCUSSION

9:30 AM PM07.01.04

Effect of Airborne Contaminants on Plasma-Induced N-Doping of Graphene Films Germain Robert Bigras, Xavier Glad, Richard Martel and Luc Stafford; Université de Montréal, Montréal, Quebec, Canada.

Graphene has been extensively studied thanks to its promises for the next generation of electronic and optoelectronic devices [1]. The availability of versatile post-processing techniques of graphene is mandatory for applications in which properties of pristine graphene are insufficient. In recent years, various methods, including plasma-based approaches, have been explored to tune the doping with nitrogen atoms of graphene films as a means of either

increasing the electron density or inducing a band gap [2]. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. Studies often blindly aim at increasing the nitrogen content while minimizing defect generation. In addition, very few measures are taken into account to control the gas phase impurities. Even for freshly grown graphene, Li et al. [3] showed that the graphene receive a strong variation of its hydrophobicity within days due to the deposition of hydrocarbons on the surface. Analysis of the N-doping dynamics must therefore discriminate if N-incorporation occurs in the airborne contaminants or in the graphene lattice itself.

In this work, we explore the potential of the late afterglow of a microwave N₂ plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils. The low ion density (< 10⁷ cm⁻³) and the high density of reactive neutrals (> 10¹⁴ cm⁻³) and metastable species (> 10¹⁰ cm⁻³) of the nitrogen late-afterglow [4] are believed to enhance chemically driven surface reactions over purely physical ion bombardment. Therefore, enhanced functionalization at the surface is expected due to interactions between nitrogen and the hydrocarbons. In addition, the tunable nature of the nitrogen afterglow allows the exposition of the sample to a continuum of environments; from damaging conditions (Early afterglow - EA) to a milder region (Late Afterglow - LA).

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/(N+C+O) = 19% for LA and 49% for EA) while RS assessed an uncommonly low damage generation (D:G < 0.4 for LA and D:G < 1.3 for EA) for such incorporation. Transfer towards SiO₂ substrate reveals the loss of a strong proportion (80%) of weakly bonded nitrogen moieties for LA-treated graphene. This can be explained by a significant incorporation of N atoms within the hydrocarbon layer.

[1] Vashist, S. K., & Luong, J. H. (2015). Carbon, 84, 519-550.

[2] M. Fan, Z. Feng, C. Zhu and al. (2016) J. Mater. Sci. 51 10323-10349.

[3] Z. Li, Y. Wang, A. Kozbial, and al. (2013) Nat. Mater. 12 925-931.

[4] Afonso Ferreira, J., Stafford, L., Leonelli, R. and al. (2014). J. of Applied Physics, 115(16), 163303.

9:45 AM PM07.01.05

Roll-to-Roll Vacuum Deposition of Polymers with In-Line Curing—A Comparison of Two Curing Sources (Plasma and Electron Beam) Carmen Alonso Herr¹ and Hazel Assender²; ¹University of Oxford, Oxford, United Kingdom.

The high-speed roll-to-roll deposition of smooth, thin layers of polymer in vacuum, by flash evaporation of the monomer followed by radiation curing, is useful for smoothing and topcoat layers (e.g. for high performance gas barrier films) as well as dielectric for capacitors and OTFTs. The properties of a diacrylate (TPGDA), deposited using different curing sources (plasma and electron beam, both which are used commercially for in-vacuum polymer layer deposition) have been studied, both with the layer attached to the polymer substrate, and by removing the thin film from the substrate to study the properties of free-standing films. The degree of cure, which determines mechanical, adhesion and stability properties for example, has been measured by FTIR-ATR and by Soxhlet extraction to reveal the relative contributions of free monomer and 'dangling ends' in the network. This degree of cure, and the film thickness (by ellipsometry), mechanical properties (by dynamic mechanical thermal analysis) and surface topography (by AFM) have been characterized as a function of process parameters, and a comparison has been made between the two curing sources. A model is proposed to describe the differences: for plasma curing density of reactive species created is independent of the layer thickness, and hence the degree of cure depends primarily upon the flux of radiation. In contrast for E-Beam cured samples, the number of reaction centres created depends primarily on the thickness of the coating. Such an understanding of the curing leads us to link the process parameters with other polymer's properties, which is relevant especially when creating multilayers such as barrier coatings or devices for organic electronics.

10:00 AM BREAK

SESSION PM07.02: Nanoparticles and Nanocrystals I

Session Chairs: Minoru Fujii and Vladimir Svrcek

Monday Morning, November 26, 2018

Hynes, Level 1, Room 107

10:30 AM *PM07.02.01

Equilibrium and Non-Equilibrium Atmospheric Plasma Routes for Nanoparticle Synthesis Matteo Gherardi^{1,2}, Vittorio Colombo^{1,2}, Marco Boselli¹, Anna Liguori¹, Romolo Laurita¹ and Tommaso Galligani¹; ¹Department of Industrial Engineering, Alma Mater Studiorum - University of Bologna, Bologna, Italy; ²Interdepartmental Center for Industrial Research in Advanced Mechanical Engineering Applications and Materials Technology, Alma Mater Studiorum - University of Bologna, Bologna, Italy.

The ever-increasing demand for high-quality nanosized materials coming from many industrial and research fields has been spurring the research on viable methods for their synthesis.

In the first part of the talk, RF inductively coupled plasmas for nanoparticle synthesis will be introduced as an effective tool for the continuous production of nanoparticles at high throughput. This technology has encountered the interest of many industrial nanoparticle producers thanks to its distinctive features such as high energy density, high chemical reactivity, high process purity, large plasma volume and long residence time; also, RF synthesis of nanoparticles benefits from the large number of available process variables (e.g. power, frequency, process gases, phase of the precursor and system geometry) that ensure the versatility of the process and from the high cooling rate (10⁴-10⁵ K/s) in the tail of the plasma, that allows to produce tailored nanoparticles with a narrow particle size distribution (PSD). During the talk, advantages and disadvantages of the technology will be introduced, focusing, in particular, on the challenges posed by up-scaling. The use of modeling instruments as supporting tools for the design and engineering of industrial-scale high-throughput thermal plasma systems for nanoparticle synthesis will be discussed [1, 2].

The second part of the talk will deal with Cold Atmospheric Plasmas (CAPs) as the centerpiece of a family of simple and environmentally friendly methods for the synthesis and modification of nanostructures in liquid environments [3]. Results highlighting the role of the chemical composition of the liquid environment (either NaCl + NaOH or NaCl only, dissolved in distilled water) on the characteristics of the produced nanoparticles will be presented. Furthermore, the possibility of synthesizing nanoparticles from a nebulized solution containing metallic salts will be discussed; an applicative example, where this process is employed to produce an antibacterial coating composed of a layer of antibacterial silver nanoparticles embedded within two polymeric thin films, will also be provided. A similar approach, simultaneously depositing silver nanoparticles and a polymeric matrix, will be presented as well [4].

[1] S. Bianconi, M. Boselli, M. Gherardi and V. Colombo: Plasma Chem. Plasma Process. 37, 3, p717-738 (2017).

[2] S. Bianconi, M. Boselli, M. Gherardi and V. Colombo: J. Phys. D: Appl. Phys. 50, 16, 165204 (2017).

[3] D. Mariotti and R. M. Sankaran: *J. Phys. D: Appl. Phys.* 44, 17, 174023 (2011).

[4] A. Liguori, E. Traldi, E. Toccaceli, R. Laurita, A. Pollicino, M. L. Focarete, V. Colombo and M. Gherardi: *Plasma Proc. Polym.* 13, 6, p. 623-632 (2017).

Work partially supported by European Union's Horizon 2020 research and innovation program under grant agreement No 646155 (INSPIRED project)

11:00 AM PM07.02.02

Ultra-Small Metallic Nanocrystals Synthesis from Solid Wire Precursors via an Atmospheric Pressure Microplasma Bruno Alessi, Atta ul Haq, Dilli Babu Padmanaban, Paul Maguire and Davide Mariotti; University of Ulster, Newtownabbey, United Kingdom.

Metal nanoparticles are interesting for a wide range of scientific fields. Particles with diameters ranging from 10 nm up to hundreds of nanometres exhibit attractive properties for various applications (e.g. catalysis, chemical sensors etc.). Some of the most studied characteristics are for instance related to the possibility of tuning localized surface plasmon resonance, which depends on the nanoparticle size, shape and surrounding environment. Meanwhile, particles with diameters below 10 nm down to and below 1 nm, approach a new regime and can in some cases associated to large molecular clusters, with properties of interest to electronics and semiconductor science. Model calculations for such metallic quantum dots predict, depending on the composition, the opening of the energy bandgap¹ and the consequent appearance of photoluminescence effects². However, most of the synthesis methods that yield narrow size distributions employ high vacuum methods or use surfactants to sterically control particle size during their synthesis.

Atmospheric pressure microplasmas recently revealed their value for nanomaterial synthesis³. Microplasmas simultaneously offer a cheap alternative to low pressure plasmas and some unique peculiarities. For example, the high ratio of energetic electrons allows activating chemical reactions which are otherwise hard to achieve. These plasmas at atmospheric pressure typically show also high electron densities and enhanced rate of ion-neutral interactions, which are mainly responsible for charging and selective heating of particles inside a plasma. The former preventing agglomeration of particles and the latter allowing to achieve higher particle temperatures compared to the gas background. A clear advantage of microplasmas for nanomaterial synthesis is the small residence time of nucleating particles inside the active plasma region, which can be reached with a flow-through type reactor. Moreover, samples can be easily prepared either as evenly dispersed colloids or as solid films of stacked particles.

In the current work, ultra-small metallic nanocrystals, or quantum dots (below 5 nm) of different elements such as tin, copper, bismuth and others have been produced with a gas phase atmospheric pressure microplasma using the corresponding solid bulk form as precursor; we discuss material characterization as well as the potential underlying mechanism of formation supported by a few different experimental plasma diagnostics.

References

1. Küfner, S., Furthmüller, J., Matthes, L., Fitzner, M. & Bechstedt, F. Structural and electronic properties of α -tin nanocrystals from first principles. *Phys. Rev. B* **87**, 235307 (2013)

2. Zheng, J., Nicovich, P. R. & Dickson, R. M. Highly Fluorescent Noble-Metal Quantum Dots. *Annu. Rev. Phys. Chem.* **58**, 409–431 (2007)

3. McKenna, J. *et al.* Synthesis and surface engineering of nanomaterials by atmospheric-pressure microplasmas. *Eur. Phys. J. Appl. Phys.* **56**, 24020 (2011)

11:15 AM PM07.02.03

Low Temperature Plasma Synthesis of III-V Stibnide and Nitride Nanocrystals from Bulk Metals Necip B. Uner and Elijah Thimsen; Washington University in St. Louis, Saint Louis, Missouri, United States.

Low temperature plasma (LTP) is a unique gas-phase synthesis tool for various forms of nanomaterials. The nonequilibrium environment in the LTPs has been utilized to synthesize many semiconductor nanocrystals in tubular flow-through reactors by using suitable vapor precursors. These materials mostly comprise Si, Ge, various sulfides and oxides. III-V semiconductors, which constitute an important family of materials for optoelectronic applications, haven't been explored as well. Although reports on the synthesis of InP and GaN have been reported, stibnides and nitrides currently don't have an established method of synthesis that yields high quality nanocrystals. In this work, we present a general plasma synthesis route for bare nanocrystals of GaSb and GaN. The method diverges from the previously reported syntheses of semiconductor nanocrystals, since use of vapor precursors is avoided. Instead, aerosols of constituent metals are generated in evaporation and condensation sources. These aerosols of Ga, Sb and gaseous nitrogen bearing species were used as precursors. Produced aerosols are mixed and then sent into a flow-through Ar LTP reactor. Aerosols vaporize inside the LTP and the generated vapor re-forms the compound semiconductor by way of nucleation and condensation [1]. Since particles obtain unipolar negative charge inside the LTP, Coulombic repulsion prevented the formation of agglomerates. Synthesized particles were verified to be free-standing and crystalline via transmission electron microscopy. Furthermore, particles were mixed on atomic scale. Stoichiometry was found to be adjustable by manipulating the input aerosol concentrations and input plasma power. In addition to results on reactor operation and on extensive *ex-situ* characterization of materials by means of electron microscopy and x-ray diffraction, functionalization of the produced nanocrystals by surfactants and the resulting photoluminescent properties of the materials will be presented.

[1] N. B. Uner and E. Thimsen, "In-Flight Size Focusing of Aerosols by a Low Temperature Plasma," *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

11:30 AM *PM07.02.04

Plasma and Laser-Assisted Synthesis and Modification of Nanoparticles in Liquids Natalie Tarasenko; B.I. Stepanov Institute of Physics National Academy of Sciences of Belarus, Minsk, Belarus.

At the present stage of nanotechnology development nanoparticles are considered as important building blocks for the construction of nanodevices with working parameters exceeding those of the bulk analogs. Therefore, to reach the distinctive properties of nanoparticles the development of the controlled synthesis procedures that enable tuning the particles parameters during the preparation is now considered to be crucial. Among the nanoparticles fabrication methods plasma-assisted techniques that imply the combination of top-down and bottom-up approaches, are considered to be promising for controlled fabrication and targeted modification of nanoparticles parameters such as size distribution, phase composition, inner structure and surface chemistry. The present paper summarizes the developed plasma and laser-assisted approaches focusing on the controlled fabrication and modification of nanoparticles of different composition and morphology.

Several plasma-assisted techniques were used in the experiments: electrical discharge in liquids, plasma generated in contact with liquid, laser ablation in liquid and laser irradiation of colloidal solutions. Studying the influence of liquid composition on the particles properties it has been found that electrical discharge and laser ablation in non-reactive liquids can be used for effective fabrication of metallic and semiconductor (Si, Ge) nanoparticles. In contrast, plasma generation in reactive liquids by electrical discharge or laser ablation can be simple but effective route for binary nanoparticles synthesis.

For the effective fabrication of composite nanoparticles the combined laser-plasma approaches have been developed. One of them is based on the sequential laser ablation of targets in liquids that can be used as a tool to prepare binary or ternary nanocomposites as well as for the doping of nanocrystals. Another route of the compound nanoparticles preparation is based on the laser treatment of the nanoparticles mixtures. Special attention has

been paid to the production of metastable alloys as their formation is favorable under the conditions of dense plasma with high temperature and pressure. For this, the combined plasma-laser approach based on electrical discharge treatment of the micropowders suspension in liquids with subsequent laser irradiation of the formed colloids has been developed that has been shown to be suitable for fabrication of Cu-Zn, Ag-Cu, Ge-Sn and Si-Sn alloys as well as binary and ternary compounds, such as Gd_3Si_4 , $Gd_3Si_2Ge_2$ and $CuInSe_2$. The surface chemistry of the prepared nanoparticles can be additionally adjusted by treatment of the prepared colloid by plasma in contact with liquid. This method was demonstrated to be effective for the improvement of the luminescent efficiency of the carbon and silicon quantum dots promising for photovoltaic and biomedical applications.

SESSION PM07.03: Silicon-Based Nanocrystals
Session Chair: Matteo Gherardi
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 107

1:30 PM *PM07.03.01

Plasma Processing and Synthesis of Silicon/Carbon Based Nanocrystals for Energy Applications Vladimir Svrcek¹, Calum McDonald¹, Marius Bürkle¹, Davide Mariotti² and Koji Matsubara¹; ¹AIST Japan, Tsukuba, Japan; ²Ulster University, Belfast, United Kingdom.

New opportunities of environmental and abundant Si- and C-materials arising thanks to the unique physical and chemical properties exhibited at quantum confinement sizes. Due to the quantum confined sizes and thus the high surface to volume ratio, the surface termination influences significantly the overall optoelectric properties of the material.

Our research showed that atmospheric plasma treatment of quantum confinement silicon and carbon achieves desired chemistry for both synthesis and surface functionalization. In particular, two different plasma-liquid systems for synthesis and/or surface engineering are discussed in details in this talk. Firstly, a femtosecond (fs) laser beam (100 fs) is used to generate a plasma in the liquid. The laser-based surface engineering method uses a pulsed laser to generate a plasma plume in the colloidal solution.

Secondly an atmospheric pressure microplasma generated under ambient air condition whereby microplasma interacts with the surface of the colloid. We show that the experimental observations are rationalized by systematic study of the size and functionalization of nanocrystals dependence of the bandgap using density functional theory calculations. In addition the characteristics of Si nanocrystals functionalized by plasma controlled surface allows a successful carbon nucleation and can be used as a non-metallic catalyst. Further more, atmospheric plasma generated by both fs laser and dc microplasma allow favorable chemistry for the synthesis of carbon nanocrystals.

The carbon nanocrystals possess surface molecular arrangements that allowed dispersed in water without any additional reagents or ligands. We demonstrate that *carbon nanocrystals* be efficiently use as the absorbing layer in solar cells. Due to the quantum confinement, a significant enhancement in term of open circuit voltage is recorded in solar cells. The result clearly show that plasma based synthesis of carbon nanocrystals offer great opportunities for high efficiency photovoltaic devices

2:00 PM PM07.03.02

Structural Characterization of Hyperdoped Silicon Nanocrystals from Nonthermal Plasmas Katharine Hunter¹, Nicholas Bedford², Katelyn Schramke¹ and Uwe R. Kortshagen¹; ¹Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States; ²Chemical Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Doped nanocrystals, while difficult or impossible to produce through conventional colloidal methods due to self-purification processes, are readily achieved in nonthermal plasmas. In this work we have investigated silicon nanocrystals doped with either boron or phosphorus synthesized in a low-pressure nonthermal discharge. Surprisingly, the mid-infrared plasmonic response of these nanocrystals reveals carrier concentrations on par with or exceeding the thermodynamic solubility limits for boron and phosphorus in bulk silicon. These elevated carrier concentrations indicate the importance of unique growth processes within the plasma environment not accessible by equilibrium methods. To begin to understand the mechanisms that enable this effective hyperdoping of silicon nanocrystals in nonthermal plasmas we have employed pair distribution function analysis of high-energy x-ray diffraction patterns, which simultaneously captures the short-range periodicity and long-range disorder inherent in these nanocrystalline systems. By running reversed Monte Carlo (RMC) simulations, which minimize the discrepancy between measured and modeled pair distribution functions, we have obtained ensemble-average nanocrystal configurations for a range of doping levels. Analysis of the structure of these model configurations provides an estimate dopant location and coordination within the nanocrystal. We find that while the majority of dopant atoms reside at or near the nanoparticle surface, a sufficient number of 4-fold coordinated dopant atoms are located within the core of the nanoparticle to explain their plasmonic resonance. Furthermore, we find that low-temperature annealing of these nanocrystals produces an apparent increase in the concentrations of dopant atoms within the nanocrystal core. K. Hunter acknowledges support by the National Science Foundation Graduate Research Fellowship Program under Grant No. 00039202. This work was supported primarily by the U.S. National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program. The use of beamline 11-ID-B of the Advanced Photon Source, a U.S. Department of Energy (DOE), Office of Science User Facility, operated for the DOE Office of Science by Argonne National Laboratory was facilitated under Contract No. DE-AC02-06CH11357.

2:15 PM PM07.03.03

Synthesis of Silicon Nanoparticles in a Low Pressure Microwave Plasma Reactor on a Pilot Plant Scale—Characterization of Particle Growth and Influence of Different Process Conditions on Particle Characteristics Frederik Kunze¹, Stefan Kuns^{2,1}, Mathias Spree¹, Tim Huelser¹, Hartmut Wiggers^{2,3} and Sophie M. Schnurre¹; ¹IUTA, Institut für Energie- und Umwelttechnik e.V., Duisburg, Germany; ²IVG, Institute for Combustion and Gas Dynamics – Reactive Fluids, University of Duisburg-Essen, Duisburg, Germany; ³CENIDE, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, Duisburg, Germany.

Within the last years, numerous research results have indicated that nano-sized silicon can be used for a multitude of different applications. Especially its size-dependent properties such as limited phonon transport (in thermoelectric devices), structural flexibility (for battery applications) or quantum-confined optical properties (for optical applications) are of high interest.

Gas-phase synthesis is a suitable method for the continuous production of high amounts of specific nanoparticles, which enables applications based on highly-pure nanostructured materials. Up to now, microwave plasma reactor processes have mainly been investigated on the laboratory scale and only a very few approaches were dealing with scaling to higher production rates. Therefore, microwave supported plasma reactors are not yet regarded as a competitive manufacturing method to produce high amounts of nanoparticles with consistent high quality.

In this work, a microwave plasma reactor is used for the generation of silicon nanoparticles from gaseous monosilane (SiH_4) at the pilot scale. The reactor uses a microwave frequency of 915 MHz and a microwave power up to 50 kW in contrast to 2.45 GHz and 6 kW on the laboratory scale. It will be shown that this reactor enables the formation of highly crystalline and either soft-agglomerated or hard-agglomerated silicon nanoparticles depending on the process conditions. In order to characterize the growth process of the particles within the plasma reactor, samples of particles were extracted directly from the gas phase at different distances from the plasma utilizing high-speed thermophoretic sampling. Furthermore, the systematic investigation of process conditions reveals that the particle size and aggregation can be independently controlled by a selective adjustment of the process conditions. It was identified that a higher gas outlet velocity of the nozzle results in a reduced residence time, thus leading to shorter growth time and smaller particles. In contrast, an increase in SiH_4 concentration up to 48 vol.% does not lead to further growth of isolated primary particles but promotes aggregate formation from smaller primary particles. In addition, it is shown that we are able to run a production process with consistently good quality of the silicon nanoparticles at high production rates of up to 200 g/h. Therefore, a full-day synthesis of silicon nanoparticles was performed. Nanoparticles were collected at fixed time intervals during the synthesis period and characterized via BET measurements and TEM images. This continuous sampling allows to detect unwanted changes of the particle characteristics during the synthesis and gives an indication of the long-term stability of the plasma process. The results indicate a stable process for many hours.

The authors gratefully acknowledge the support by the German research foundation (DFG) in scope of the research group 2284 "Model-based scalable gas-phase synthesis of complex nanoparticles".

2:30 PM *PM07.03.04

Boron and Phosphorus Co-Doped Colloidal Silicon Quantum Dots Minoru Fujii, Hiroshi Sugimoto and Shinya Kano; Kobe University, Kobe, Japan.

A colloidal solution of Si quantum dots (QDs) is a versatile material for electronics, optoelectronics and biophotonics. Recently, we have developed a new type of all-inorganic Si QDs that can be dispersed in alcohol and water almost perfectly without organic ligands, and exhibit size-dependent luminescence in the near-infrared range in water. The unique property of the QDs arises from the unique structure. The QD has a core-shell structure; the core is heavily B and P codoped crystalline Si and the shell is an amorphous layer composed of B, Si and P. The shell induces negative potential on the surface and prevents agglomeration of Si QDs in polar solvents. Furthermore, isolation of an exciton in a crystalline core from environment by the shell makes the luminescence insensitive to the change of the environment and robust for chemical treatments. To the ligand-free surface of codoped Si QDs, molecules in a solution can access easily, and thus a variety of charge-transfer-induced processes such as a photocatalytic effect and chemical doping are expected. In this presentation, we first discuss the structure of codoped Si QDs based on the data obtained by atom probe tomography and transmission electron microscopy. We then discuss the size dependence of the energy state structure, especially that of the donor and acceptor levels, based on the data obtained by scanning tunneling spectroscopy, photoemission yield spectroscopy and photoluminescence spectroscopy. We then discuss charge transfer interaction between Si QDs and adsorbed molecules, including the photocatalytic activity and chemical doping. We show the formation of a variety of nanocomposites composed of codoped Si QDs and noble metal nanostructures, and discuss the enhanced optical responses due to the coupling with the localized surface plasmon resonances of metal nanostructures. Finally, we discuss the electrical transport property of a Si QDs film produced from the colloidal solution and demonstrate the possible application as electronic devices.

3:00 PM BREAK

SESSION PM07.04: Thin Films, Coatings and ALD I

Session Chairs: David Graves and Chi-Chin Wu

Monday Afternoon, November 26, 2018

Hynes, Level 1, Room 107

3:30 PM *PM07.04.01

Low Resistivity HfN_x Layers by Plasma-Assisted ALD with External rf Substrate Biasing Mariadriana Creatore; Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands.

In this contribution I will discuss the deposition of HfN_x by means of plasma-assisted ALD. The process adopts tris(dimethylamino)cyclopentadienylhafnium [$\text{CpHf}(\text{NMe}_2)_3$] as Hf precursor and H_2 or Ar/H_2 plasmas as reducing co-reactant. Films are found to exhibit an electrical resistivity of $9.0 \times 10^{-1} \Omega\text{cm}$, in the absence of external substrate biasing [1]. The latter is attributed to the presence of oxygen in the film up to 20 at%, which is responsible for a limited Hf^{3+} fraction of 0.65. First-principles DFT calculations are adopted to explore the underlying mechanisms of O incorporation: chemisorption of H_2O from the reactor background on the bare HfN surface is kinetically and thermodynamically highly feasible, and leads to Hf-OH surface groups.

A steady decrease in electrical resistivity down to $3.3 \times 10^{-3} \Omega\text{cm}$ is observed upon increasing the substrate potential up to -130 V by externally biasing the substrate [2]. The variations in electrical resistivity with the potential correlate with the extent of grain boundary scattering in the films, which significantly decreased upon increasing the potential up to -130 V. The latter is primarily due to major changes in the film chemical composition, namely the decrease in O content to less than 2 at% for a potential of -130 V and an associated increase in the Hf^{3+} fraction up to 0.82. In parallel, DFT calculations reveal that cationic species present in H_2 plasma are highly reactive towards the surface -OH groups.

An increase in the energy of bombarding cations promotes the dissociation of Hf-OH surface bonds, followed by H_2O formation and desorption. When heavier and more energetic ion bombardment (as generated in an Ar/H_2 plasma) is applied, the electrical resistivity goes down to $4.1 \times 10^{-4} \Omega\text{cm}$. It is worth noting that such low resistivity is achieved for films as thin as ~35 nm. Next to a high $\text{Hf}(\text{III})$ oxidation state fraction of 0.86 ± 0.02 , the key towards the very low resistivity is the suppression of in-grain defect density and nano-porosity in HfN_x films.

Overall, the application of a substrate potential is shown to highly affect the chemical composition, microstructure and the associated electrical properties of the HfN_x layers.

[1] Karwal et al., J. Vac. Sci. Technol. A, 01B129 (2017)

[2] Karwal et al., J. Mat. Chem.C 6, 3917 (2018)

4:00 PM PM07.04.02

Synthesis of Layered Sulfide Heterostructures via RF Sputtering Dennice M. Roberts^{1,2}, Sage Bauers² and Andriy Zakutayev²; ¹University of Colorado-Boulder, Boulder, Colorado, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States.

Deposition of layered chalcogenide materials allows for generation of novel material systems with tunable optical and electronic properties sensitive to changes in both dimensionality and the stacking sequence of constituent compounds. Synthesis of kinetically-controlled products can be achieved by the deposition of an amorphous “initial state” in which thickness and composition are precisely controlled, thus enabling rational study of structure-property relationships as a given material progresses from a monolayer to a more bulk-like state. To date, only selenide and telluride thin films have been demonstrated in this vein. We show the first synthesis of sulfide materials assembled under this framework and generate heterostructures comprised of alternating layers of crystalline MoS₂ and SnS. RF sputtering is utilized to generate thin films of amorphous material in which layer-by-layer control of thickness and composition enables kinetic control over stacking sequence and phase of constituent layers. We discuss the design, synthesis, and optimization techniques necessary to form precursor and crystalline end states. Film microstructure is visualized using transmission electron microscopy and structure determinations are made using x-ray reflectivity and diffractometry techniques to determine information about overall heterostructure orientation and constituent material phases.

4:15 PM PM07.04.03

AlN Etching Under ICP Cl₂/BCl₃/Ar Plasma Mixture—Experimental Characterization and Plasma Kinetic Modeling Mohammad Rammal^{1,2}, Ahmed Rhallabi^{1,2}, Delphine Néel³, Dalila Make³, Alexandre Shen³ and Abdou Djouadi^{1,2}; ¹Institut des Matériaux Jean Rouxel, Nantes, France; ²University of Nantes, Nantes, France; ³III-V Lab, Palaiseau, France.

AlN is one of the III-V materials used in a new generation of electronic and optoelectronic devices especially in high power devices. Indeed, thanks to its good conductivity, it is well qualified to evacuate heat from the devices and thus improves their performance and reliability. One of the challenges is to succeed in the pattern transferring from the mask to AlN material using plasma etching process. Chlorinated plasmas are well tested to etch AlN material. Some studies show that chlorinated plasmas containing only molecular chlorine or with argon is not efficient to properly success the etching step in terms of selectivity, anisotropy and surface roughness. The addition of BCl₃ seems to improve the performance of the AlN etching. However, it remains difficult to find the optimal operating conditions that improve the morphological properties of etched AlN structures. In this context, we present experimental results of AlN etching using ICP BCl₃/Cl₂/Ar plasma mixture. The AlN is deposited on Si and InP substrate using DC magnetron sputtering. Then, a SiO₂ patterned hard mask is used to have a selective etching. The etch rate reached is 200 nm/min; with a small problem of microtrenching and a sidewall angle of 75°. This problem can be overcome using simulation in which the optimum etching conditions can be found. In parallel, plasma kinetic model of BCl₃/Cl₂/Ar is developed to study the effects of the reactor parameters such as RF power, pressure and gas flow rates on the neutral and charged species evolution as well as the electron temperature and density. The model is based on the 0D global kinetic model. Mass balance equations of 34 neutrals, negative and positive ions coupled to the charge neutrality equation and power balance equation are established to quantify the species densities and their fluxes onto the substrate surface. Particular attention is given to the analysis of the percentage of BCl₃ gas effect on the reactive species densities involved in the etching processes such as the positive ion and atomic chlorine densities.

4:30 PM *PM07.04.04

Surface Reactions During Plasma-Assisted Atomic Layer Deposition of SiN_x Sumit Agarwal; Colorado School of Mines, Golden, Colorado, United States.

The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for novel atomic layer deposition (ALD) processes for a variety of materials including Si-based dielectrics such as SiN_x. Development of new ALD techniques that can meet the demands for semiconductor manufacturing requires an atomistic level understanding of the surface reaction processes. In our lab, we use in situ optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALD.

In this presentation, I will discuss the low-temperature plasma-assisted ALD of SiN_x films where one of the key challenges has been to grow conformal films in high-aspect-ratio nanostructures such that the sidewall structure and composition is the same as the top surface. I will discuss the surface reactions that occur during ALD of SiN_x using chlorosilanes and aminosilanes as the Si precursors with an NH₃ and N₂ plasma, respectively, as the nitrogen source. The NH₃-plasma based processes show >95% conformality, but the wet-etch rate in dilute HF is much higher for the sidewalls compared to the planar surface. While N₂ plasma based processes show a low wet-etch rate for both the sidewalls and the planar surface, the conformality is ~50%. Based on these observations, we have developed a new three-step ALD process for SiN_x growth using Si₂Cl₆ followed by CH₃NH₂, and then an N₂ plasma. I will show that in this three-step ALD process because nitrogen is supplied to the surface partially in a thermal step followed by an N₂ plasma, the films are more conformal with a sidewall wet etch rate that is intermediate between NH₃ and N₂ plasma based ALD processes.

SESSION PM07.05: Optical, Electrical and Other Properties
Session Chairs: Michael Gordon and Y Raitzes
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 107

8:30 AM *PM07.05.01

Bottom up Synthesis and Optoelectrical Application of Suspended Graphene Nanoribbon Arrays in Wafer Scale Toshiaki Kato and Toshiro Kaneko; Tohoku University, Sendai, Japan.

Graphene nanoribbons (GNRs) combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. However, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. We have developed a new, simple, scalable method based on novel plasma catalytic reaction [1-4] for directly fabricating narrow GNRs devices with a clear transport gap [5]. Since the establishment of our novel GNR fabrication method, direct conversion of a Ni nanobar to a suspended GNR is now possible. Indeed, GNRs can be grown at any desired position on an insulating substrate without any post-growth treatment, and the wafer-scale synthesis of suspended GNR arrays with a very high yield (over 98%) is realized [6]. The growth dynamics of suspended GNR is also investigated through the systematic experimental study combined with molecular dynamics simulation and theoretical calculations for phase diagram analysis. The improvement of thermal stability of Ni nanobar can be a key to realize the GNR nucleation in our method, which can be given by supplying higher density of carbon from plasma to liquid-phase Ni nanobar. The wettability of liquid-phase Ni nanobar against to the SiO₂ substrate is also found to be an important factor forming the suspended structure of GNR. It is also revealed that the minimum length of

GNR can be decided by the wavelength of Plateau-Rayleigh instability known as a traditional instability of fluid flow. Furthermore, unique optoelectrical property, known as persistent photoconductivity (PPC), is also observed in our suspended GNR devices. By using the PPC, GNR-based non-volatile memory operation is demonstrated. We believe that our results can contribute to pushing the study of atomically thin layered materials from basic science into a new stage related to the optoelectrical applications [7-9] in industrial scale.

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9:00 AM PM07.05.02

Optical-Erasable TiO₂ Non-Volatile Memory Using Deep Trap Charges Taeyoon Kim^{1,2}, Jung Wook Lim^{1,2}, Seong Hyun Lee¹, Jeho Na¹, Jiwoon Jeong¹, Kwang Hoon Jung^{1,2}, Gayoung Kim^{1,2} and Sun Jin Yun^{1,2}; ¹ICT Materials Research Group, Materials & Components Basic Research Division, Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of); ²Advanced Device Engineering, University of Science and Technology, Daejeon, Korea (the Republic of).

Recently, oxide-based metal-oxide-semiconductor field-effect transistors (MOSFETs) have been actively studied for the applications of non-volatile memory devices in transparent and flexible electronic products. Oxide-MOSFETs have much lower off-state leakage current than Si-MOSFETs, allowing low-power memory operation, and further advantages such as good uniformity, low process temperature, and high transmittance in the visible wavelength range. Conventional oxide-based non-volatile memory generally uses positive and negative gate voltage (V_G) pulses to achieve the program and erase states, respectively. However, the n-type nature of most oxide semiconductors makes it difficult to conduct sufficient amounts of holes in the channel oxides, leading to a high power consumption and long erase times; thus input power sources (e.g. light) in addition to voltage are required. In a memory device, the difference between the programming and erasing voltages is known as the “memory window”. In a non-volatile memory, the memory window should be set to secure a sufficient margin of read voltage (V_{read}) for stable device operation; wider memory windows can be achieved with more defect sites trapping more charges. However, shallow traps among the defect sites adversely affect device stability. Therefore, it is necessary to selectively exclude shallow trap sites to satisfy both a wide memory window and high device stability.

In this work, we propose TiO₂ MOSFET-based non-volatile memory device, employing the deep trap interface (DI) sites as a simple floating gate without tunneling oxide. For the fabrication of TiO₂ MOSFET, 80 nm-thick Al₂O₃ gate dielectric layer and 30 nm-thick TiO₂ films were deposited by plasma enhanced atomic layer deposition on a n⁺ Si wafer which plays a role of back gate. In order to demonstrate performance of TiO₂ MOSFET, we measured electrical characteristics of the fabricated devices in the dark and violet light (VL)-irradiated conditions at 25 °C. For VL irradiation, we used standard LEDs (center wavelength of 400 nm) as a light source with an incident power of 0.13 W/cm². This device demonstrated a high on/off ratio of 10⁷ and a sizable memory window due to deep traps at the interface between Al₂O₃ and TiO₂. Interestingly, irradiation with 400 nm VL could completely restore the program state to the initial state (performing an erasing process) owing to the visible light-sensitive TiO₂ channel. Device reproducibility was greatly enhanced by selectively passivating shallow traps using an in-situ H₂-plasma treatment. The passivated memory device showed a highly reproducible memory window and on-state current even during a retention bake test at 85 °C. We expect that our simple-structured TiO₂-based non-volatile memory device, which is completely erasable only by light irradiation and shows reproducible and stable operation, will usefully employed in a wide range of future electronic devices.

9:15 AM PM07.05.03

Impact of CMOS TiN Metal Gate Process on Microstructure and Its Correlation with Electrical Properties Pushpendra Kumar^{1,2,3}, Florian Domengie¹, Charles Leroux², Patrice Gergaud² and Gerard Ghibaudo³; ¹STMicroelectronics, Crolles, France; ²CEA-LETI, Grenoble, France; ³Université Grenoble Alpes, Grenoble, France.

TiN metal gate has been introduced in advanced CMOS devices for its advantages such as eliminating Fermi level pinning and phonon scattering, but it also introduces the metal gate granularity due to multiple crystal orientations. This may impact device electrical and physical properties, such as effective workfunction W_{eff} , threshold voltage local variability σV_{TH} , mechanical stress and sheet resistance. σV_{TH} might be reduced by reducing the TiN grain size or by obtaining a unique crystal orientation and so we have focused on identifying TiN metal gate process conditions that can achieve this goal. Hence, the impact of RF Physical Vapor Deposition (RF-PVD) parameters, Ar pressure and RF power, on the preferred orientations and size of the TiN crystallites is investigated.

28nm CMOS FDSOI HKMG stack was deposited, consisting of 1 nm SiO₂ interfacial layer, 1.8 nm HfSiON High-k layer and 5 nm TiN gate deposited by RF-PVD with combined DC and RF generators. TiN is formed by reactive sputtering of a pure Ti target in a nitrogen-containing ambient of Ar&N₂. Ar pressure and RF power were varied over a wide range. The preferred orientations and grain size are determined by X-Ray Diffraction (XRD), in out of plane (0-20) and in-plane configurations respectively. Sheet resistance is measured by 4 probe method and thickness by X-ray-reflectometry (XRR) to calculate TiN deposition rates. Mechanical stress was calculated by applying Stoney's equation and Ti/N ratio is measured by X-ray fluorescence (XRF). It is observed that as Ar pressure decreases and RF power increases, average grain size, % TiN <200>/TiN <111>, deposition rate and film mechanical stress increases. For 3 conditions a unique TiN grain orientation is obtained. As the RF power increase and pressure decrease, the number of Ar⁺ ions and number and energy of sputtered Ti atoms increase. Increased Ti atoms energy enhances crystal growth and favors the preferred orientation <200>, having the lowest energy. Increased Ar⁺ ions, due to channeling effect, enhances crystallization and will re-sputter TiN <111> crystals more than <200>. Increase in Ar⁺ and Ti number and energy will result in denser films due to peening effect, thus increasing the stress. TiN sheet resistance follows an inverse power law as the grain size is decreased due to an increase in grain boundaries.

EOT and W_{eff} were extracted by fitting CV measurements with Poisson Schrödinger simulations for devices with varying EOT. Extrapolation of W_{eff} to EOT=0 gives intrinsic TiN workfunction (W_{Fm}) + dipoles at SiO₂/high-k interface (δ). W_{Fm} change is expected to depend on the % of <200> (W_{Fm} =4.6eV) or <111> (W_{Fm} =4.4eV). The electrical extraction of $W_{Fm} + \delta$ evidences an opposite trend. Our results strongly suggest that W_{Fm} expected shift is hidden by an opposite effect at the SiO₂/high-k interface due to the sensitivity of its dipole to TiN process. The Ti/N ratio is playing a major role with a suppression of dipole δ for Ti rich gates.

9:30 AM PM07.05.04

Physical Vapor Deposition, Wet Etch, Plasma Treatment and Material Exploration for Advanced Packaging Application Prayudi Lianto; Applied Materials, Singapore, Singapore.

Advanced packaging requires ever-increasing I/O counts which calls for shrinkage in the Cu interconnect dimension while meeting device performance and reliability. In Applied Materials, we are enabling fine line/spacing (L/S) Cu redistribution line (RDL) by scaling the barrier thickness, controlling amount of wet etch critical dimension (CD) loss and undercut, developing plasma surface treatment to meet electrical performance specs, and exploring new material with better barrier property. We demonstrated end-pointed Ti etch process with 10nm Ti barrier thickness to reduce undercut from >300nm to <20nm and extend RDL scaling to sub-2um regime. Step coverage is not compromised with such thin barrier as demonstrated by successful plating on topography features. With end-pointed Cu etch process, we were also able to reduce Cu CD loss from >0.3um to <0.1um and reduce line resistance non-uniformity from >1mOhm to <0.5mOhm. We established the importance of plasma treatment to lower RDL electrical leakage from >1mA to <1nA. Low leakage is critical to minimize device power dissipation.

9:45 AM PM07.05.05

Synthesis of Hybridised Silicon Nanospheres with Functionalisation by Modified ML-PECVD [Jonathon Mitchell](#); Koriyama, Japan.

The fabrication of hybridised silicon nanospheres by simplified plasma-enhanced chemical vapour deposition (PECVD) without the need for seed particle injection or microwave plasma has been improved upon by applying a modified multi-layer deposition technique (ML-PECVD). In this, we have incorporated our method for fabricating the hybridised nanospheres with the topical advantage presented by the ML-PECVD method for active functionalisation of the particles within the plasma itself. Additionally, we have improved the active control of nanospheres during plasma formation utilising our proprietary spectroscopic imaging system.

As the physiochemical properties of nanoparticles depend on their size and shape, isolation within a suitable matrix permits single-particle analysis and experimentation, overcoming averaging effects. Following suspension in ethyl acetate, analysis of the multisublattice ordering was observed by SEM, μ RAMAN and plasmonic nanospectroscopy on both crystalline silicon (c-Si) and semiconductor polymer substrates. While c-Si acts as a suitable measurement surface, our interest is aimed at the inclusion of the hybridised nanospheres to flexible opto-electronic devices. To this extent, suitable pairing between the nanosphere and polymer functionalisation states are desired. Typically, this must be done ex-situ of the deposition process, however, our method utilised exchange bias effects with suitable semiconductor polymer substrates within the deposition chamber during deposition. This presents a promising methodology for the rapid fabrication of active opto-electronic materials while removing extensive chemical processing between fabrication layers.

10:00 AM BREAK

SESSION PM07.06: Energy, Catalysis and Interfaces I
Session Chairs: Bruce Koel and Mohan Sankaran
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 107

10:30 AM *PM07.06.01

Gas-Surface Reactivity of Vibrationally Excited Molecules—Energetics, Dynamics, and Their Significance in Interfacial Reactivity [Arthur Utz](#); Tufts University, Medford, Massachusetts, United States.

Vibrationally excited molecules exhibit enhanced reactivity in the gas phase and on surfaces. In high temperature or plasma processing environments where they are abundant, they are potentially important, or even dominant contributors to chemical reactivity. This talk will highlight state-resolved gas-surface scattering experiments that use infrared laser excitation of molecules in a supersonic molecular beam to quantify a molecule's reaction probability as a function of its incident kinetic, vibrational and rotational energy and quantum state. The experiments quantify how effectively vibrational energy promotes a molecule's dissociative chemisorption probability on the surface, and how that efficacy varies with the energy and the character (e.g. bend vs. stretch) of the molecule's vibrational motion. We find that the reactivity of individual molecules is strongly influenced by the dynamics of the molecule-surface collision. Vibrational mode-selective chemistry, in which reaction probability, S_0 , depends on the molecule's vibrational motion, and not just its energy, and bond selective reactivity, in which a localized vibrational excitation dictates which bond breaks, are the rule, rather than the exception in our studies of methane dissociation on Ni and Ir surfaces. These markedly non-statistical reactivity patterns result from the limited duration of the methane molecule-surface collision, and the resulting constraint on the time available for significant energy redistribution within the reaction complex. A consideration of the rates and pathways for vibrational energy flow within the reaction complex provides a qualitative picture for predicting the extent of non-statistical behavior that might be expected in more complex reactive systems.

The ability to control precisely and independently how energy is partitioned among translational, rotational, and vibrational motion of the gas-phase molecule and surface atom excitation allows us to explore chemical reactivity over a wide range of strongly non-thermal conditions. These measurements have proven to be invaluable benchmarks for testing and validating the absolute accuracy of DFT-based electronic structure calculations. Varying surface temperature for a fixed energetic configuration of the gas-phase reagent reveals a dramatic surface temperature enhancement that is most pronounced near the energy threshold for reaction. Coverage-dependent measurements of reactivity show how the surface-bound carbon products of methane's dissociation can initially enhance, and then inhibit further methane activation on Ni(111).

11:00 AM PM07.06.02

Nonthermal Plasma Enabled Catalysis of Greenhouse Gas Zunrong Shen, Seigo Kameshima, Kenta Sakata and [Tomohiro Nozaki](#); Department of Mechanical Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Nonthermal plasma-assisted reaction enhancement mechanism in porous Ni/Al₂O₃ catalysts (3-mm spherical pellets) in CH₄/CO₂ conversion was investigated. Dielectric Barrier Discharge (DBD) was employed for this purpose. In the plasma catalysis, carbon filaments were deposited only on the external surface of catalyst pellets, providing the clear evidence that the DBD and catalyst interaction is possible only in the external surface of the pellets: neither generation of DBD nor the diffusion of excited species in the internal micropores is possible. Meanwhile, coke distribution over the pellet cross-section revealed the coke formation in the internal micropores was diminished dramatically by DBD, although plasma and catalyst interaction is limited only in the external surface. We also found that the external surface of catalyst pellets was oxidized exclusively by DBD, forming NiO shell with thickness of ca. 20 micrometers: Ni catalyst was not oxidized in the thermal catalysis regime. Such unique reaction behavior is explained by the catalyst effectiveness factor. The reactivity of plasma generated species is so high that the surface reaction of those species completed at the external surface of pellets: Carbon deposition and oxidation cycle is accelerated by the plasma generated reactive species at the external surface of pellets, while those species do not diffuse

towards internal micropores.

According to the molecular beam experiments, vibrationally excited CH₄ is known to promote dissociative chemisorption over the metal surface. Although vibrationally excited species have yet to be identified experimentally in the high-pressure nonthermal plasma system, the numerical simulation of one-dimensional streamer type discharge plasma (typical in DBD) predicted that the vibrationally excited CH₄ is the most abundant and long-lived species produced by low energy electron impact. Likewise, vibrationally excited CO₂ and H₂O are expected to promote catalytic surface reactions; nonthermal plasma is the viable and economical approach to generate copious amount of vibrational species at low temperature. Based on these ideas, nonthermal plasma enabled greenhouse gas conversion was diagnosed by temperature programmed reaction spectrometry as well as materials characterization by XRD and Raman spectroscopy. Moreover, carbon deposition and Ni catalyst oxidation behavior was correlated in the plasma- and thermal-catalysis regime, enabling clear insight into the reaction enhancement mechanism induced by nonthermal plasma. The reaction enhancement mechanism were further discussed in relation to vibrationally excited species.

11:15 AM PM07.06.03

Microplasmas Synthesis of Nanoscale Zinc Oxide Tetrapods – Crystal Growth and Optical Properties Dilli Babu Padmanaban, Darragh Carolan, Bruno Alessi, Conor Rocks, Paul Maguire and Davide Mariotti; Plasma Science and Nanoscale Engineering group, NIBEC, Ulster University, Belfast, United Kingdom.

Due to their higher specific surface area, nanoscale structured materials possess excellent optoelectronic properties [De Mello Donegá C, 2014]. Here in our work, we demonstrate the synthesis of nanoscale zinc oxide tetrapods (ZnO-TPs) from zinc metal wire in ambient air using an atmospheric pressure microplasma technique. The ZnO-TPs were characterised for crystal structure (scanning electron microscopy, transmission electron microscopy and x-ray diffraction), chemical composition (x-ray photoelectron spectroscopy) and optical properties (ultraviolet-visible spectroscopy, photoluminescence). The ZnO-TPs consist of tetragonally placed arms each of about 65 nm length and 11 nm diameter; these particles are further classified as wurtzite phase with each arm particularly grown along the (0002) plane containing polar surfaces. The lattice parameters of the crystals were evaluated using Rietveld refinement procedure [Luca Lutterotti, 1999]. The analysis of optical properties shows that the ZnO-TPs exhibit sharp absorption near the ultraviolet region of the electromagnetic spectrum due to direct band electronic transition. Photoluminescence shows a strong ultraviolet emission due to band to band transition and with a weak visible-violet emission due to interface traps or interstitial Zn metals. Phase purity is confirmed by XPS and x-ray crystal diffraction measurements. Overall, the characterization shows that ZnO-TPs crystals are free from its oxygen vacancies. The formation mechanism of ZnO-TPs in the plasma is initially characterized by sputtering of metal atoms from the Zn solid wire precursor. The interaction of the plasma afterglow with the surrounding air contributes to reacting of the plasma product with air oxygen and fast quenching. While nitrogen does not contribute to the chemistry of the ZnO-TPs, there is evidence that it plays a crucial role in determining the quality of nanocrystals produced. We finally demonstrate the applicability of the plasma process in the fabrication of solar cells, where ZnO-TPs were used as the electron transport layer for devices with methyl ammonium lead iodide perovskite as the absorber.

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11:30 AM *PM07.06.04

Understanding of Plasma Catalysis form Surface Streamer Propagation Hyun-Ha Kim; AIST, Tsukuba, Japan.

Plasma chemistry has been the subject of considerable studies due to the intrinsic characteristics brought by highly non-equilibrium state and high reactivity of chemical species. These characteristic properties include ultra-fast reaction time ($\sim 10^{-4}$ s), mild reaction condition (ambient pressure and temperature), and rapid start-up/ shutoff. Plasma-catalysis, which combines nonthermal plasma with various catalysts, is based on the bilateral interaction. The potential applications of plasma-catalysis include hazardous VOCs removal, NOx removal, ammonia synthesis, CO₂ conversion, and fuel reforming. Many of synergistic effects have been reported by many researcher groups in the past 10 years. However, the degree of enhancements seems to be dependent on the type of combinations (i.e. reactor configuration, power supply, type of catalysts, and operating conditions). In this regard, fundamental studies are necessary to accelerate the broad use of plasma-catalysis in many industrial fields. Our recent study on the time-resolved ICCD imaging of surface streamer provided different nature of streamer depending on the polarity of applied voltage. Especially, a counter-propagating cathode-directed streamer initiated from ground electrode (anode) was appeared. This presentation will cover from the current understanding the interaction of plasma and catalyst to the possible applications in various chemical reactions.

Acknowledgements

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SESSION PM07.07: Energy, Catalysis and Interfaces II
Session Chairs: Hyun-Ha Kim and Arthur Utz
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 107

1:30 PM *PM07.07.01

Plasma-Enhanced Chemical Conversions of CH₄, CO₂ and N₂ in Hybrid Plasma-Catalysis DBD Reactors—The Role of Catalysts Xiaofang Yang, Yiguang Ju and Bruce E. Koel; Princeton University, Princeton, New Jersey, United States.

Non-equilibrium plasmas have been explored for chemical conversion of stable gases, e.g., CO₂, CH₄, and N₂, and synthesis of carbon materials because of

the high activity of electronically and vibrationally excited species produced during plasma discharge. However, these active species are highly energetic, favoring bond-breaking rather than bond forming reactions. For example, commonly in plasma alone conditions CO₂ reforming of methane produces CO and H₂ and ammonia (NH₃) synthesis has low conversion. Introducing catalysts into the plasma may change the activity and selectivity, but also disturb the plasma discharge. Thus, a significant challenge in plasma-catalysis hybrid systems is to achieve the strongest synergistic interactions between the plasma and catalyst to increase the selectivity for desired reaction pathways, e.g., methane coupling. We report on two types of dielectric barrier discharge (DBD) reactors (with a coaxial tube and parallel plates) that have been used to screen catalytic effects of different metal surfaces and supported catalysts in plasma-catalysis hybrid systems. We observed strong synergistic effects between non-equilibrium plasma and catalysts for both methane coupling and NH₃ synthesis reactions. First, in CO₂ reforming of methane in the co-axial reactor, we found that the reaction activity and selectivity strongly depend on the catalyst and reaction conditions. Under thermal only conditions, PtFe/Al₂O₃ catalyzed mainly the formation of CO and H₂, but with the plasma on, the selectivity shifted to methane coupling reactions. Interestingly, an Ag/Al₂O₃ catalyst with an AC discharge demonstrated 100% selectivity to CH₄ coupling reactions at 350 °C. This strongly suggests that the reaction selectivity can be controlled by using appropriate catalysts and plasma discharge energy. Methane coupling using the plasma-catalysis reactor at low temperatures and pressures mainly produced higher hydrocarbons, suggesting a potential route for converting cheap and abundant methane gas into high value hydrocarbons and fuels. Secondly, we also compared the performance for ammonia synthesis of catalysts using active metals (Pd, Pt, and Fe) or less active metals (Au, Ag, and Cu) or their alloys. In the parallel plate hybrid reactor, we found that the metal-nitrogen (M-N) bond energy was not the only parameter governing the catalytic activity for NH₃ synthesis in plasma. Better catalytic activity could be achieved by bimetallic catalysts that contained catalytic sites for both N₂* dissociation and hydrogenation of M-N bonds, leading to our observations of a highly active PdFe catalyst for NH₃ synthesis in plasma.

2:00 PM PM07.07.02

Atmospheric Plasma Surface Functionalization of Aluminum Nanoparticles as Novel Energetic Materials Chi-Chin Wu¹, Kelsea Miller², Shancita Islam² and Michelle Pantoya²; ¹U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States; ²Mechanical Engineering, Texas Tech University, Lubbock, Texas, United States.

Aluminum-based nanoparticle (nano-Al) additives have the potential to enhance the performance of explosives/propellants due to their high energy content and potentially rapid burning enabled by the exceptionally large specific surface area. When incorporated into explosive formulations, nano-Al can theoretically release two to three times more energy as conventional CHNO-based explosives. However, the parasitic alumina (Al₂O₃) shell typically coating Al particles both consumes a significant portion of the nano-Al, lowering its energy content, and acts as a diffusion barrier for the unreacted Al core, leading to reduced energy release. The higher surface energy of alumina also causes the metal nanoclusters to aggregate and develop into oxide-covered large agglomerates that further exacerbate their inactivity. This work describes our explorations of passivating and functionalizing the outermost shell of aluminum nanoparticles with different coatings, including carbon-based structures and energetic salts such as aluminum iodate hexahydrate (AIH). Our approach exploits custom-designed atmospheric non-thermal plasma dielectric barrier discharge (DBD) reactors to functionalize the fuel particle surface. Using aluminum nanoparticles of 80 nm average size as an example, the particle surface is successfully engineered and becomes carbon-rich when using carbon monoxide plasma gas. On the other hand, the particles are covered with a layer of AIH crystals after treatment with an inert gas plasma followed by immersion in the iodate acidic solution. Transmission electron microscopy images exhibit high crystallinity in the outer shell for plasma-functionalized particles for both carbon- and AIH-wrapped aluminum nanoparticles with low agglomeration. This work demonstrates the potential to alter the surface of metallic nanoparticles with tunable surface properties via tuning the conditions of atmospheric plasmas.

2:15 PM PM07.07.03

Plasma-Enhanced Chemical Film Conversion (PECFC)—A Metal-Free, Low-Temperature Approach to Synthesizing Continuous, Large-Area Layered Material Films Tianqi Liu¹, Yongkun Sui², Haithem A. Mustafa^{3,4}, Ozan Akkus^{3,4}, Christian A. Zorman² and Mohan Sankaran¹; ¹Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, Ohio, United States; ²Electrical Engineering and Computer Science, Case Western Reserve University, Cleveland, Ohio, United States; ³Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, Ohio, United States; ⁴Center for Applied Raman Spectroscopy, Case Western Reserve University, Cleveland, Ohio, United States.

Thin films of crystalline materials are typically synthesized by thermally decomposing vapor precursors at the surface of a catalytic substrate.[1] A plasma enables the process temperature to be lowered by assisting in decomposition of the precursor molecule through gas-phase excitation as in the case of plasma-enhanced chemical vapor deposition (PECVD) [2] and plasma-enhanced atomic layer deposition (PEALD).[3] Here, we report another plasma-assisted approach to synthesizing thin films which we term plasma-enhanced chemical film conversion (PECFC).[4] Molecular precursors are first prepared as a thin film on a substrate by solution methods, and subsequently converted by a combination of heating and plasma treatment. In comparison to other thin film techniques, our approach circumvents the adsorption step to promote nucleation and reduce substrate interactions, allowing direct growth on metal-free substrates which eliminates the need for transfer. Additionally, the approach is additive, reducing materials wastage and producing materials at the point-of-need including patterned structures.

Two examples of thin film materials will be presented that demonstrate the capabilities of this synthesis approach: hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS₂), both of which are layered materials and can be produced atomically thin. To synthesize h-BN, a single-molecular precursor, ammonia borane, is initially prepared as a thin film by spray deposition, spin coating, or ink-jet printing, and subsequently converted in a cold-wall reactor with a planar, atmospheric-pressure dielectric barrier discharge. We performed a systematic study of h-BN growth with plasma-assisted heating and heating alone. Micro Raman spectroscopy shows that the minimum nucleation temperature is lowered from 800 to 500 °C by the addition of a plasma. From the full-width-half-maximum (FWHM) of the E_{2g} Raman scattering peak characteristic of h-BN, we also find that the crystal domain size is larger with a plasma. From capacitor devices, the dielectric properties of the synthesized h-BN are found to be improved with a plasma from a relative permittivity of ~2.8 to the near-bulk value of ~3.7. To synthesize MoS₂, a similar approach of converting its corresponding single-molecule precursor, ammonium tetrathiomolybdate with a plasma has been studied. In this case, a single-step conversion leads to a rough, nanostructured film. Adding a second thermal annealing produces a very smooth (RMS < 0.5 nm) and continuous film. We will discuss potential superior properties of these films over exfoliated and CVD-grown films, as well as preliminary studies of their applications as electrocatalysts and transistor elements.

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2:30 PM BREAK

3:00 PM *PM07.08.01

Microplasma Jet Spray Deposition of Nanostructured Materials for Energy Applications Michael Gordon; Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

The ability to synthesize a wide range of nanostructured materials, as well as integrate them into larger systems, is fundamental to the development of next-generation micro- and optoelectronic devices, sensors, and energy harvesting and storage technologies. Toward this goal, we have developed a versatile, plasma spray-like deposition technique, based on flow-through hollow cathode discharges at 10-100 Torr (microplasma jets), that can deposit nanoparticles, dense layers, and structured thin films of crystalline materials on virtually any surface (e.g., conductors, insulators, polymers, fibers, and lithographic patterns). A supersonic microplasma jet is seeded with organometallic precursors under reducing or oxidizing conditions to create a directed flux of growth species (e.g., atoms, ions, clusters, and/or nanoparticles) that are subsequently 'spray-deposited' onto the surface of interest at room temperature. A diverse range of nanostructured materials, e.g., metals (Cu, Ni, Pd), oxides (CuO, ZnO, MnO₂, RuO₂, NiO, Fe₂O₃, Co_xO_y), doped oxides (Fe_xNi_{1-x}O), and spinels (NiFe₂O₄), with different morphologies (nanoparticles, dense columnar films, or hierarchical nanostructures, etc.) can be realized with the technique. Applications to be discussed include Fe-doped NiO and NiFe₂O₄ for electrocatalysis (OER); NiO and Co_xO_y for supercapacitors; and combining microplasma spray deposition with photolithography and lift-off to create MnO₂ and RuO₂-based microsupercapacitors for on-chip energy storage.

3:30 PM PM07.08.02

One-Pot Synthesis of Boron Nitride Nanotube/Metal-Ceramic Hybrids by Thermal Plasma Keun Su Kim^{1,2}, Homin Shin¹, Martin Couillard¹, Mark Plunkett¹, Dean Ruth¹, Christopher Kingston¹ and Benoit Simard¹; ¹National Research Council Canada, Ottawa, Ontario, Canada; ²Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, Canada.

Boron nitride nanotubes (BNNTs) are nano-sized rolled-up cylinders of single- or few-layered hexagonal BN sheets. Thanks to their ultra-strong impact resistance and lightweight, BNNT-metal or ceramic nanocomposites are highly promising in the development of advanced hard armours such as anti-ballistic body armours or armoured vehicles¹; however, developments of such composites have been significantly hampered by the low reactivity of pristine BNNTs towards metal or ceramic matrices, as well as by the complexity and inefficiency of BNNT functionalization *via* multistep post-processing. To address this issue, we have developed a new plasma process in which growth of BNNTs and their subsequent surface modification (e.g., doping or decoration) with metal or ceramic nanoparticles occur in a same reactor. The density functional theory (DFT) study was performed first to gain insights into stable structures of BNNT/metal-ceramic hybrids and their reaction stoichiometry. Based on the theoretical predictions, synthesis experiments were conducted with different additive particles such as AlN, TiN, and Cu in order to provide different reactivity to BNNTs. The morphological properties and chemical compositions of the products were assessed by various characterization techniques including SEM, TEM, TGA, FT-IR, UV-Vis, and XRD. The results of optical emission spectroscopy (OES) and 2D thermo-fluid modelling studies will be also presented to discuss the growth mechanism of those hybrid materials in this plasma process.

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3:45 PM PM07.08.03

Growth and Characterization of Nano-Platelet IrO_x Films Milena B. Graziano³, Brendan Hanrahan³, Thomas C. Parker², David Baker³, Bradley Sanchez^{1,3}, Manuel Rivas^{4,3,5} and Paul Sunal³; ¹University of Maryland, College Park, Maryland, United States; ²Aberdeen Proving Ground, Aberdeen, Maryland, United States; ³U.S. Army Research Laboratory, Adelphi, Maryland, United States; ⁴University of Connecticut, Storrs, Connecticut, United States; ⁵General Technical Services, LLC, Wall, New Jersey, United States.

Iridium oxide (IrO_x) is a well investigated compound with superb physical and electrical properties that have proven advantageous to numerous medical, electrochemical, and microelectronic systems. Its vast applicability is attributed to its versatility and ease of fabrication using common deposition techniques, such as reactive sputtering. This method is extensively reported in literature, as films can be readily grown under Ar/O₂ mixed atmospheres and film properties can be controlled by fixing the gas mixing ratio. Interestingly, a large increase in the O₂ gas flow results in a characteristic change in the film microstructure towards randomly oriented dendritic or plate-like features of high aspect ratio. Yet, no explanation to this date has been offered on how the film is produced. Since nanostructured morphologies can prove beneficial to increase the active area of IrO₂-based electrodes, this study focuses on understanding the growth mechanism, evolving microstructure, chemistry, and structural traits of reactively sputtered nano-platelet IrO_x films. IrO_x thin films were prepared by reactive DC sputtering of an Ir metal target in a mixed Ar and O₂ atmosphere. The O₂ gas flow was varied from 0 sccm to 100 sccm, while the substrate temperature and Ar flow were kept constant. At 0 sccm, polycrystalline Ir metal coatings were achieved, displaying a strong (111) polycrystalline texture and a uniform surface structure comprised of small fibrous grains. An increase to 60 sccm leads to the formation of (110) and (220)-oriented rutile IrO₂ large grains, densely packed to form a columnar film microstructure. At and above 80 sccm, the films exhibit significant loss of crystalline perfection and mechanical strength due to the formation of non-stoichiometric, (101)-oriented IrO_x nano-platelets. Results indicate that the nano-platelets begin to grow locally on a (110)-oriented IrO₂ thin layer and extend along their vertical axis before they populate the entire layer surface. The growth of nano-platelets is the result of high energy, overstoichiometric IrO_x compound species produced due to the adsorbed oxygen at the Ir metal target surface. These atoms bombard the growing (110) IrO₂ film surface and incorporate into less dense (101) atomic planes. This produces a sudden shift in the film texture and a significant decrease in the film density and crystallinity. All observations indicate that the growth evolution and orientation of the IrO_x nano-platelets is not a consequence of strain effects, as the films are reproducible on other substrate surfaces, including Ir, Cr, SiO₂, PZT, and photoresist. Furthermore, the nano-platelet films exhibit low resistivity and low reflectivity, desirable for pyroelectric devices and solar water-splitting applications. As such, the use of nano-platelet IrO_x films could prove instrumental to novel device designs that require large surface area, anti-reflective, low resistivity electrodes.

4:00 PM *PM07.08.04

Towards Selective Synthesis of Boron Nitride Nanotubes by Arc Discharge—Experiments and Simulations Y. Raites², Shurik Yatom², Rachel Selinsky¹, Yao-Wen Yeh¹, Predrag Krstic³, Biswajit Santra¹, Longtao Han³, Alexander Khrabry², Igor Kaganovich², Bruce E. Koel¹ and Roberto Car¹; ¹Princeton University, Princeton, New Jersey, United States; ²Princeton Plasma Physics Laboratory, Princeton, New Jersey, United States; ³Stony Brook University, The State University of New York, Stony Brook, New York, United States.

This work reviews the results of recent studies on the synthesis of boron nitride nanotubes (BNNTs) in an anodic arc discharge at near atmospheric pressure of nitrogen and nitrogen-rich gas mixtures. These results shed light on a number of fundamental aspects of BNNT synthesis by thermal and near-thermal plasmas generated by arcs [1] and plasma torches [2], including the role of metal catalysis [1] and the importance of high temperature arc environments (> 2000 K) [3], synthesis selectivity [2,5], and growth mechanisms [5,6]. In our experiments, the boron feedstock was provided through arc ablation of either a boron-rich anode electrode or a pure boron target immersed into the arc plasma [5,7]. The arc was characterized using optical emission spectroscopy, high speed imaging, and electrical measurements [7,8]. The synthesized products collected from the arc chamber were evaluated *ex-situ* using standard material characterization techniques. The results of experiments demonstrate that the arc plasma composition includes boron and nitrogen species. Transition metals such as W, Ni, Co were also observed in the emission spectrum whenever they were included in the electrode material compositions. *Ex-situ* evaluation showed that BNNTs synthesized with and without Ni and Co have generally similar quality and are primarily single and double-walled independent of the presence or absence of these metals in the arc and nanotubes. Moreover, we did not observe W in the synthesized BNNTs collected from the arc reactor post-run even when it was present in the arc emission spectrum during the arc run. These results suggest that in contrast to what has previously been hypothesized, namely that metal catalysts are needed for the growth of BNNTs in the arc [1] we obtained no evidence of this need. Instead, we propose that similar to plasma torch synthesis [2], arc synthesis can sustain metal-free growth of BNNTs. Experiments have also confirmed recent predictions of molecular dynamics simulations that the addition of hydrogen to the arc in a pure nitrogen atmosphere can be an effective way to control the synthesis selectivity of boron nitride nanomaterials [4]. We also observed BNNTs attached to boron nanoparticles supporting a root-growth mechanism for their formation consistent with recent ab initio molecular dynamics simulations [5]. However, we have not observed boron particles for the majority of collected nanotubes leaving open the possibility of alternative growth mechanisms [3,6].

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4:30 PM PM07.08.05

The Combination of Atmospheric-Pressure Plasma and Digital Finishing for the Creation of Novel Hydrophilic and Hydrophobic Patterning Carrie Cornelius; APJet, Inc., Morrisville, North Carolina, United States.

Cold plasma consists of electrons, ions, excited atoms and molecules, neutral gas species, and UV radiation that occur at low temperatures and can be used to initiate chemical reactions. Often plasma treatment is carried out in high vacuum, low-pressure devices. Vacuum plasma treatment allows plasma particles to achieve large mean free paths and results in very energetic ions and electrons capable of rapid and extreme surface modification and highly successful chemical grafting. However, low-pressure devices are most suitable for batch processing of substrates. They require long pump down times and have a limited volume per batch. Therefore, the integration of these devices into a continuous industrial manufacturing process is not readily achievable. Atmospheric-pressure plasma, as used in this research, allows for the continuous treatment and curing of substrates and transforms an otherwise costly and small-batch technology into a commercially viable approach for high-volume processing. Despite the lower mean free paths of atmospheric plasma systems, proper selection of processing parameters and working gas can be used to successfully induce chemical reactions. These chemical reactions include the polymerization of monomers and their attachment to material substrates. The use of cold atmospheric-pressure plasma to induce chemical reactions eliminates the need for heat, allowing for heat-sensitive materials to be processed and coated with desired functional finishes. These high-performance coatings can add attributes to the finished goods such as high levels of water and oil repellency. In this work, advances in the curing capabilities of cold atmospheric-pressure plasma technology are combined with inkjet printing of plasma-polymerizable chemicals to pattern hydrophobic chemistry and hydrophilic chemistry onto substrates. These multi-functional patterns impart unique material properties and aesthetics, including the ability to readily create channels that can direct and move fluids. The polymerization of the chemical coating is examined as well as the ability of the printed repellent coating to transport various types of fluids. The influence of the structure and surface energy of the starting substrate is also identified as a key variable in determining effectiveness of the transport properties.

SESSION PM07.09: Poster Session: Plasma-Based Synthesis, Processing and Characterization of Novel Materials for Advanced Applications

Session Chairs: Tomohiro Nozaki and Mohan Sankaran

Tuesday Afternoon, November 27, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

PM07.09.01

Surface Treatment Against Process Oxidation of Ultra-Thin Silver Films Soroush Hafezian, Rodrigue Béaini, Ludvik Martinu and Stéphane Kéna-Cohen; École Polytechnique de Montréal, Montreal, Quebec, Canada.

Metallic transparent conductors play an important role in modern optoelectronic devices and as heat-reflectors in energy saving applications. Their high conductivity and high transparency for thicknesses below a few nanometers are crucial for device functionality. In particular, silver thin films demonstrate very high sheet conductivity shortly after percolating as well as a neutral transmitted color. Moreover, silver can easily be scaled to coat large surfaces with the help of physical vapour deposition techniques such as magnetron sputtering, providing nanoscale uniformity over a few square meters. Silver, however, is extremely sensitive to reactive oxygen and requires special precautions in reactive plasma-based processes. One strategy for protecting silver thin films is to have a thinner (~3 nm) metallic film (here Ti) as protective layer. As the silver/barrier double-layer is exposed to the O_2 plasma, reactive species diffuse through the Ti barrier layer which gradually transforms into a film of TiO_x . This metal-oxide layer eventually self-passivates and blocks oxygen diffusion. However, in the presence of oxygen and ultraviolet radiation, if the barrier thickness is not adequate or if the oxidation process is too severe, reactive species can diffuse through the barrier and lead to film failure.

In this work, we characterize the degradation mechanism of silver at the interface with the barrier and present a solution to reduce and prevent the process

oxidation of silver in a reactive environment. We first compare the growth of silver films deposited by magnetron sputtering on glass, ZnO and (3-Mercaptopropyl)trimethoxysilane (MPTMS) treated glass. The bare glass and ZnO film represent a case of physisorption with low and high surface energy, respectively. Higher surface energies tend to reduce the mobility of sputtered silver atoms and lead to early coalescence. The MPTMS-treated glass, thanks to the thiol bond formation, represents a case of chemisorption process where the incoming silver atoms are attached to the sulfur available on the surface. Samples are covered with a 2-nm barrier titanium film and exposed to reactive O₂ plasma. XPS and TOF-SIMS analysis on the samples reveal that the degradation process starts with the migration of silver through the top titanium barrier. We quantify the degradation by comparing the atomic content of silver present at the very top of the degraded samples. We find that in the case of the ZnO and glass substrates there is a much higher amount of silver migrating through the top barrier to the surface compared to the MPTMS-treated glass. We attribute this difference of migration to the sulfur-silver bonds provided by the MPTMS monolayer.

PM07.09.02

Universal High-Resolution Surface-Structuring Technique for Fabricating Complex 3D Nanopatterns by Plasma Process and Its Application in Display Devices Hwan-Jin Jeon; Department of Chemical Engineering and Biotechnology, Korea Polytechnic University, Siheung-si, Korea (the Republic of).

High-resolution, high-aspect-ratio nanostructure patterning technology has the potential to be of significant value in various fields such as nanoelectronics, optics, biosensors, energy devices, and display devices owing to the optical and electric peculiarities of nanostructured materials. Lots of approaches, which include nanoimprint, photo-, interference- soft-, edge-, colloidal lithography and electron-beam assisted deposition, have been studied to achieve 3D 10 nm-scale features.

Recently, we introduced a new surface nanostructuring technique termed "secondary sputtering lithography (SSL)", which enables the fabrication of 10 nm-scale ultrahigh-resolution 3D patterned structures of substrate surface with high aspect ratios over large areas by utilizing secondary sputtering phenomena during plasma ion etching process. This new technique utilizes the secondary sputtering phenomenon, wherein target material particles are emitted by accelerated Ar⁺ ions over a large angular distribution, leading to the fabrication of 10nm scale high-resolution patterns without complicated equipment. We have successfully created various nanostructures on a 10 nm-scale, including ultrathin lines, hole-cylinders, and honeycomb structure. We have also applied ~10nm-scale line patterns with a high aspect ratio to align liquid crystal molecules. High-resolution patterning (~20 nm) of indium-tin-oxide (ITO) surface layers with a high aspect ratio (~10) was successfully carried out without damage to the electrical/optical properties of the ITO, and the patterned ITO could function as a bifunctional conductive alignment layer for liquid crystal devices without a conventional polymer alignment layer fabrication process.

PM07.09.03

VHF Plasma CVD Synthesis of Photochromic ZnO Nanocrystal Hiroshi Kajiyama¹, Shin Kuboyama², Hiroki Uyama¹, Atsushi Otomo³, Shuhei Inoue³, Yukihiko Matsumura³, Keiji Takata⁴ and Kiichiro Uchino²; ¹Tokushima Bunri University, Sanuki-shi, Japan; ²Kyushu University, Kasuga-shi, Japan; ³Hiroshima University, Higashi-Hiroshima-shi, Japan; ⁴Kansai University, Suita-shi, Japan.

Zinc oxide (ZnO) is a promising material for ultraviolet optical devices, especially in light emitting diodes and lasers. In this study, it is shown that ZnO nanocrystal synthesized by a VHF plasma CVD process is a photochromic material. The structural and electronic properties of PC states are investigated.

We developed a VHF (80MHz) plasma CVD apparatus, which could hold stable plasma with a high electron density and low electron energy at the pressures up to 100 Pa. Because of this, the growth of nanocrystals in a vapor phase is greatly promoted. For the ZnO synthesis, a vapor of Zn(C₂H₅)₂ was introduced to a VHF plasma of a gas mixture of argon (Ar) and oxygen (O₂). The ZnO film was formed on an unheated substrate. The film was exposed to UV lights and annealed at various temperatures. An x-ray absorption fine structure (XAFS) measurement was done to analyze the changes of local structures.

The *as grown* films were transparent. An AFM observation showed that the films consisted of ball-like nanocrystal with a diameter of 60-120 nm. The gas pressure during the plasma synthesis was a few hundred Pa. A substrate was not heated. Therefore, it is plausible to consider that crystal growth completed in a vapor phase.

The transparent film (*as grown*) changed to dark color by UV (254 nm) irradiation in an ambient air at 300 K. This is the PC transition of ZnO nanocrystal. The PC states were quite stable at the temperatures up to 500 K. At 550 K, however, the color gradually changed back to transparent like *as grown* films.

The transparent film once experienced PC transition again changed to PC states by UV irradiation. However, the PC films annealed at 600 K never changed to PC states. It is noteworthy that the temperature range existed for the PC stability. This indicates that ZnO nanocrystal were in a non-equilibrium phase in terms of crystallinity.

The XAFS analysis revealed that a Zn-Zn bond length of PC sample was longer by 0.015 nm compared to *as grown* sample. At the same time, the absorption edge energy shifted to higher by 5 eV, which indicate that a Zn valence changed to 2+ δ from 2. This is an evidence that electron were accumulated by UV irradiation.

In summary, ZnO nanocrystal was synthesized by using a VHF plasma CVD apparatus. It was confirmed that the PC transition of ZnO nanocrystal accompanied the changes in terms of local structures and electronic states. Electron storage is the most interesting property. We are aiming to control those electrons towards a potential application such as secondary battery.

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PM07.09.04

A Novel Process to Fabricate Functional Oxide Thin Film—Hybrid Method of Atmospheric-Pressure Plasma and Chemical Solution Deposition Processes Yoshiki Shimizu¹ and Yukiya Hakuta²; ¹Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ²Advanced Operando-Measurement Technology Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology, Kashiwa, Japan.

Oxide thin films have created considerable interest because of the potential applications to such as electronic and optical devices. Up to now, various deposition methods have been developed. In the past decade and so, simple and safe method is demanded from the viewpoint of environmental harmony, cost-effectiveness and so on. In plasma processing, atmospheric-pressure plasma (APP) is expected to meet the demands, and the application to chemical vapor deposition (CVD) performed in ambient air have been intensively studied.

This paper presents a novel method for oxide thin film fabrication involving APP process. We are investigating the hybrid method of APP and chemical solution deposition (CSD) processes. In conventional CSD process, chemical solution (CS), which is a raw material of the film, is coated on a substrate,

and then the resultant wet film is dried and converted to well-crystallized oxide thin film by heat treatment using an electric furnace or UV light sources. In our investigation, it is novel to employ APP irradiation in the dry and crystallization of the wet film. The APP irradiation is expected to lead speeding up and lowering temperature of the processing in comparison with the conventional heat treatment, owing to high reactivity of plasma.

In this presentation, we report the fabrication of zinc-oxide (ZnO) thin film, and discuss the effect of the APP irradiation based on results about the following items: a) crystallinity, b) Zn/O stoichiometric ratio, c) surface morphology, d) optical property., e) electric resistnace. Then we clarify the advantage of the APP irradiation in comparison with conventional heat treatment.

PM07.09.05

Plasma Enhanced Processing of Ge Films on Silicon as a Virtual Substrate for Lattice Matched GaAs Growth Ghada H. Dushaq¹, Ammar Nayfeh² and Mahmoud Rasras¹; ¹Engineering, New York University, Abu Dhabi, Abu Dhabi, United Arab Emirates; ²Electrical Engineering and Computer Science, Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates.

Direct growth of germanium (Ge) on silicon (Si) substrate is a key approach for the development of future high-speed photonics and electronic devices. Germanium is an ideal template for growing GaAs due to the lattice match. This will enable the fabrication of tandem solar cell and GaAs based photodetectors on low cost Si platform. While the lattice mismatch between GaAs material and Ge is significantly low compared to GaAs directly on Si, the considerable lattice mismatch of ~4.2% between Si and Ge must be considered to grow high quality Ge layers on Si and enable its use for high quality GaAs growth. Several research groups have reported high quality Ge layers on Si, however, temperatures as high as 650 C were used in performing the epitaxial deposition, also post annealing process is required. Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) has an advantage of depositing Ge at 400 C. The plasma power in RF-PECVD system acts as another energy source that stimulates energetic ions and free radicals to be deposited on the surface of the wafer at lower temperature.

In this work, we present a direct growth mechanism of thin Ge-on-Si films at low temperature using RF-PECVD. These films will be used as a template to initiate GaAs growth for heterojunction solar cells. A two-step temperature technique and different GeH₄ flow rates have been employed during the deposition process as the following: step one (low temperature (LT), high rate (HR)) the deposition was performed at 350 C with 3 sccm flow of GeH₄. In step two (high temperature (HT), low rate (LR)) of the Ge deposition the growth is carried out at 500 C with 1 sccm of GeH₄. The results show that this optimized growth limits the defect nucleation or dislocation misfit to 50 nm at the Si/Ge interface. Moreover, the measured threading dislocation density (TDD) of 700 nm thick Ge films is ~1x10⁶ cm⁻² which paves the way to achieve high quality growth of GaAs for solar cells. After this, the RF-PECVD grown Ge film on Si is used as a virtual substrate to initiate GaAs growth.

The epitaxial growth of GaAs is performed in an Aixtron close-coupled showerhead metal-organic chemical vapor deposition (MOCVD) reactor. In order to mitigate the problem of polar/nonpolar low-mismatch GaAs-Ge interface, Ge surface baking at 400 C and 700 C for 5min and 10min, respectively has been carried out. The growth of GaAs is based on two-step method. The structural properties of the GaAs layer are studied using HRSEM with EDX and cross sectional TEM. High- Resolution TEM images show high-quality Ge/ GaAs interface where no anti domain interfaces are seen. This might be attributed to the embedded Ge nanocrystals that results from RF-PECVD growth. In the context of these findings the produced "virtual" Ge substrates for GaAs growth can provide a robust method for scaleable integration of high performance III-V photovoltaics devices with large area Si wafers.

PM07.09.06

Microplasma-Assisted Synthesis of Core-Shell Au@Ag Bimetallic Nanoparticles for SERS Applications Guan-Jun Chen and Wei-Hung Chiang; National Taiwan University of Science and Technology, Taipei, Taiwan.

Surface enhanced Raman scattering (SERS) is a promising technology for various applications including plasmonic devices, photo energy generation and conversion, biomedical detection and chemical sensing. Gold-Silver core-shell bimetallic nanoparticles are extensively used in SERS, due to the unique localized surface plasmon resonance (LSPR) property [1]. Au@Ag allow tuning the physical and chemical properties through the composition and radius ratio of the core and the shell can produce strong excitation and scattering spectra than pure Ag and Au nanoparticles. Therefore, Au@Ag have attracted great attention in material science, surface science, and biological analysis by SERS. To synthesize this attracted material, seed-mediated growth is the most widely used method. However, this conventional approach is usually time-consuming and laborious.

Here we present a facile synthesis of Au@Ag bimetallic nanoparticles using a novel atmospheric-pressure microplasma-assisted electrochemistry. Microplasmas are defined as gaseous discharges formed in electrode geometries where at least one dimension is less than 1mm. Due to surface volume change, microplasmas can be operated stably with an aqueous solution as an electrode at atmospheric pressure. Energetic species formed in the microplasma is capable of initiating electrochemical reactions and nucleating particles in solution without chemical reducing agents [2]. In our experiments result, we found Au@Ag bimetallic NPs can be a synthesis in a minute time scale. The as-produced samples were extensively characterized by TEM, XRD, Raman, XPS and UV-Vis spectroscopy. We further systematic studied the Raman response of variety the molar ratio of the Au-Ag bimetallic nanoparticle using Rhodamine 6G (R6G) as the Raman probe molecules. The result indicates that the special ratio of Au@Ag bimetallic nanostructure gives significant enhancement of SERS signal than pure Au, Ag nanoparticle in similar size and verify ratio of Au/Ag will induce different SERS performance.

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PM07.09.07

Effects of Nitrogen Impurity on Sputtering Growth of ZnO Films on Si(111) Substrates Soichiro Muraoka, Jiahao Lyu, Daisuke Yamashita, Kunihiro Kamataki, Kazunori Koga, Masaharu Shiratani and Naho Itagaki; Kyushu University, Fukuoka-shi, Japan.

ZnO is a multi-functional material with a distinctive property set and a wide range of existing and emerging applications. We have recently developed a fabrication method of high-quality ZnO films employing magnetron sputtering, "nitrogen mediated crystallization (NMC)", where crystal nucleation and the growth are controlled via absorption-desorption behavior of nitrogen "impurities" [1-4]. By utilizing the films grown via NMC as buffer layers, single crystalline ZnO films with atomically flat surface have been successfully fabricated on 18%-lattice mismatched sapphire substrates. Here, we employ 15%-lattice mismatched Si(111) substrates, which offer significant advantages in terms of cost, wafer size, and electrical and thermal conductivity, for NMC growth of ZnO and see what happens if nitrogen impurity is added into the growth atmosphere.

First, 10-nm-thick NMC buffer layers were deposited on Si(111) substrates by RF magnetron sputtering in Ar/N₂ atmosphere. The substrate temperature was 750°C, and the total gas pressure was 0.35 Pa. Next, 1-μm-thick ZnO films were fabricated on NMC buffer layers by RF magnetron sputtering in Ar/O₂ atmosphere. The substrate temperature was 700°C, and the total gas pressure was 0.70 Pa.

We observed NMC method leads to significant change in the grain size of buffer layers. The average grain size derived from AFM images jumps from 9.2 to 24 nm by adding N₂ gas into sputtering atmosphere. The analysis on height-height correlation function (HHCF) indicates that N₂ addition causes an increase in the lateral correlation length ξ , a measure of migration length of adatoms, from 15 to 29 nm. Such enhanced migration allows adatoms to reach

the thermodynamically favored lattice positions, and thus leads to the large grain size as well as to high crystal quality of the films deposited on them. In fact, we observed high quality of ZnO film on NMC-ZnO buffer layer, where the full width at half maximum (FWHM) of (002) rocking curve is 0.67° , one-fourth of that for the films fabricated without buffer layers. The crystal quality has been further improved by introducing 1-nm-thick AlN layers prior to NMC-buffer layer deposition. The FWHM of ZnO film on AlN/NMC-ZnO double-layer is significantly small of 0.50° , attributed to AlN layer protecting Si surface against oxidation and thus promoting epitaxial growth of ZnO on the surface. We believe that the high-quality ZnO films obtained in this study will open up a new avenue for ZnO-based devices on Si substrates that would have a great impact on Si integrated circuit technology. This work was supported by JSPS KAKENHI Grant Number 18H01206JP, Samco Science and Technology Foundation, and NTT collaborative research.

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PM07.09.08

Electrical Property Change of Transparent Doped ZnO by Zn Addition and Desorption Yasuji Yamada¹, Shuhei Funaki¹, Orkut Sancakoglu^{1,2} and Rei Sugiura¹; ¹Shimane University, Matsue, Japan; ²Dokuz Eylul University, Izmir, Turkey.

Doped ZnO films show low electrical resistivity comparable to indium-tin oxide films and is suitable for transparent electrodes. To obtain a high performance in opto-electrical properties, many deposition studies have been conducted. However, optimum conditions have not been revealed because electrical properties vary with deposition method, equipment and even position in a deposited film. This is because crystalline defects that deteriorate electrical properties are not revealed and controlled completely. In a planner magnetron sputtering method, suppression of electrical conductivity happens at the deposition position facing the erosion area on the target. This suppression is caused by the positional distribution of crystalline defects induced by the incidence of high-energy particles coming from the erosion area.

To reveal the critical defect types to affect electrical properties of doped ZnO film, we have studied the property change of the films with different structures that provide different state and amount of Zn vacancy in the crystal after high temperature annealing. Three types of film structures of Ga-doped ZnO (GZO) were prepared by RF magnetron sputtering method at room temperature. One of the types is a simple monolayer of GZO on a glass substrate. Second one is SiO₂/GZO layered structure. Third one is a zinc inserted GZO film, SiO₂/GZO/Zn/GZO. For the GZO layer deposition, the substrates were placed on a substrate holder parallel to the target. Typical GZO thickness was 200 nm. SiO₂ capping layers were deposited also by RF magnetron sputtering with the thickness of 70 nm. Zn metal layers were deposited 6 nm in thickness between two 100 nm-thick GZO layers.

GZO monolayer films showed resistivity about $1 \times 10^{-3} \Omega \text{cm}$ after deposition. As the films annealed at 500°C for 30 min in vacuum, the resistivity decreased due to the improvement of crystalline perfection. However, annealing for longer times and at higher temperatures caused apparent increase of resistivity and decrease of carrier density. On the other hand, SiO₂-capped GZO films showed no significant change in carrier density after long and high temperature annealing. These behaviors indicate that Zn desorption from GZO lattice creates defects that reduce carrier density.

Zn inserted GZO films showed slightly decreased resistivity after the deposition and as they were annealed resistivity was further reduced to $3 \times 10^{-4} \Omega \text{cm}$. In addition, Zn inserted films exhibited no difference in resistivity between films deposited at center and erosion positions. Increase in carrier density and homogenization in resistivity by the enrichment of Zn atoms in GZO lattice can be explained by Zn vacancy. Inhomogeneous distribution of Zn vacancies existed in the as-deposited films trap electron carriers and decrease of Zn vacancies improves electrical properties. The results obtained in this study contain revealing information on crystalline defects that control properties of doped ZnO films.

PM07.09.09

Catalyst-Free Growth of C-Axis Aligned (ZnO)_{0.79}(InN)_{0.21} Nanorods by RF Magnetron Sputtering Nanoka Miyahara, Daisuke Yamashita, Daisuke Nakamura, Kazunori Koga, Masaharu Shiratani and Naho Itagaki, Kyushu University, Fukuoka, Japan.

We present catalyst-free growth of (ZnO)_{0.79}(InN)_{0.21} nanorods on c-plane sapphire substrate by RF magnetron sputtering. (ZnO)_x(InN)_{1-x} (called ZION hereafter) is a new semiconducting material, a pseudo-binary alloy of wurtzite ZnO and wurtzite InN [1-3]. This ZION has a tunable band gap over the entire visible spectrum and a high optical absorption coefficient of 10^5 cm^{-1} , making ZION a promising material for solar cells and light emitting devices. Here, we report for the first time c-axis aligned ZION nanorods where the one-dimensional structures should bring about superior electronic/photonic properties.

ZION films were deposited at 450°C by RF magnetron sputtering on c-plane sapphire substrates. O₂, N₂ and Ar gases were used and the total pressure was 0.5 Pa. The gas flow rate of O₂, N₂ and Ar were 1.8, 24.0, and 30.2 sccm, respectively. ZnO and In targets with a purity of 99.99% were used. Here, no intentional catalyst was employed. ZION films grow epitaxially on the sapphire substrates, confirmed by X-ray diffraction (XRD). The film thickness was 316 nm. The chemical composition ratio of ZION films was (ZnO)_{0.79}(InN)_{0.21}. The crystal structure of ZION films was examined by XRD. The surface morphology was evaluated by atomic force microscopy (AFM). Photoluminescence (PL) measurements were performed with a cw He-Cd laser (325 nm, 6 mW).

AFM analysis revealed that after growth of 100 nm-thick ZION film, many nanorods initiate from the surface without any intentional addition of catalyst, resulting in 100–200-nm-diameter nanorods. The symmetric XRD pattern shows a diffraction peak at 33.2° , assigned to the ZION (002) plane, and no other peaks were observed in the angular range between 20.0° and 60.0° . Thus, the ZION nanorods fabricated on the c-plane sapphire are oriented along the c-axis. The ZION nanorods show blue and red photoluminescence at room temperature. The blue emission is attributed to the band-edge emission through the recombination of free excitons and donor-bond excitons. Since crystal defects such as grain boundaries, dislocations, and zinc-vacancy-related complex are the origins of non-radiative recombination centers, we consider that the high crystal quality of ZION nanorods brings about the blue emission. On the other hand, the red emission, the intensity of which depends on the excited position of the film, is related to deep level emission through oxygen interstitial, suggesting inhomogeneous distribution of oxygen-related defects. Further discussion on the origin of PL as well as the growth mechanism of ZION nanorods will be held at the meeting.

This work was supported by JSPS KAKENHI Grant Number 18H01206, Samco Science and Technology Foundation, and NTT collaborative research.

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PM07.09.10

Investigation on Photovoltaic Properties of Nb-Doped MoS₂ Thin Films Grown by Magnetron Sputtering Seyed A. Shahahmadi^{1,2}, Siti Z. Othman¹, Puvaneswaran Chelvanathan³, Halina Misran¹, Md. Akhtaruzzaman³ and Nowshad Amin^{1,2}; ¹Institute of Sustainable Energy, Universiti Tenaga Nasional, Kajang, Malaysia; ²Electrical Electronic and Systems Engineering, Universiti Kebangsaan Malaysia, Bangi, Malaysia; ³Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi, Malaysia.

In this study, the effect of niobium (Nb) on properties of molybdenum disulfide (MoS₂) thin film absorber layer is investigated. So far, MoS₂ (0.6-20 nm) mono-layers have got the most interest for nanoscale electronic devices. However, properties of MoS₂ thin films (> 50 nm) have not been explored in details for photovoltaic (PV) applications. Hence, various films (up to 150 nm) such as un-doped MoS₂, MoS₂:Nb (0.05%), and MoS₂:Nb (0.5%) are deposited by radio frequency magnetron sputtering to investigate the usage as PV materials. These films are also subjected to dynamic sulfurization process at 550°C for 90 min to improve the crystallinity and optoelectronic properties. Results from field emission scanning electron microscope (FESEM) show similar surface morphology in all samples and the tendency for vertical lamellae growth that represents type-1 layered structure. Moreover, it is found that the thickness of the as-deposited samples increased about 50 nm after sulfurization probably due to the volumetric expansion. Structural properties are characterized by grazing incidence X-ray diffraction and it is found that the films exhibit dominant diffraction peak corresponding to (101) plane at $2\theta = 33.7$ degree, which also points to the lamellae structure as observed earlier in FESEM images. Transmittance and absorbance are obtained by UV-VIS-IR spectrometer in the range of 300–2500 nm. It is found that sulfurization leads to the emergence of a peak at 1062 nm in the transmittance spectra, besides the increase of average transmittance (300-1300 nm) from 30% to 44% for as-deposited MoS₂. The peak position shifts to higher energies (up to 794 nm) as the Nb increases, which is correlated to the changes in band structure. Carrier concentration, mobility, and resistivity are obtained from Hall measurement and n-type semiconducting properties are detected in all samples. Hole concentration drops from 10^{20} cm^{-3} to 10^{15} cm^{-3} after sulfurization while mobility increases from 0.035 to 22.6 cm^2/Vs for as-deposited MoS₂. The increase of Nb reduces the resistivity of the as-grown films from 6.78 to 4.9 $\Omega\cdot\text{cm}$ and similar trend is also attained for sulfurized MoS₂ films.

PM07.09.11

Electrical and Optical Studies of Ga-Doped ZnO Films Grown by Reactive Co-Sputtering of Zn and GaAs Shravan Kumar Appani, Samanth V Rayapati and S.S. Major; Indian Institute of Technology Bombay, Mumbai, India.

Ga-doped ZnO (GZO) films were deposited by reactive magnetron co-sputtering of zinc and GaAs (~3% of the area of erosion track) in Ar-O₂ mixture. This work focuses on the role of oxygen percentage (4–10 %) in sputtering atmosphere and substrate temperature (350 °C to 500 °C) in controlling the electrical and optical properties and investigating free carrier effects in heavily doped GZO films. XRD studies show that all the films display single wurtzite phase of ZnO with nearly complete c-axis orientation and practically negligible strain. The conducting GZO films deposited at 375 °C with less than 6% O₂ in sputtering atmosphere display resistivity of (7-13) $\times 10^{-4} \Omega\cdot\text{cm}$, carrier concentration of (7.1-11.5) $\times 10^{20} \text{ cm}^{-3}$ and Hall mobility of (5.5-8.7) $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and show marginally superior electrical parameters, just below the critical threshold value of 6% O₂ in sputtering atmosphere. With increase of O₂ in sputtering atmosphere to 6%, the films display a drastic increase in resistivity from $\sim 10^{-3} \Omega\cdot\text{cm}$ to $\sim 3 \Omega\cdot\text{cm}$, owing to significant lowering of carrier concentration below 10^{19} cm^{-3} and mobility to the range of 0.2-0.3 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. XPS studies reveal the presence of Ga³⁺ state in all the films but the incorporation of Ga decreases significantly from 2 at.% to 0.4 at.%, with increase of O₂ in sputtering atmosphere from 5% to 6%. The electrical parameters of conducting GZO films deposited with ~5% O₂ in sputtering atmosphere show a significant dependence on substrate temperature. With increase in substrate temperature from 350 °C to 500 °C, the resistivity increased monotonously from $\sim 2 \times 10^{-3} \Omega\cdot\text{cm}$ to $\sim 10^{-2} \Omega\cdot\text{cm}$. Correspondingly, the carrier concentration decreased from $\sim 1 \times 10^{21} \text{ cm}^{-3}$ to $\sim 3 \times 10^{20} \text{ cm}^{-3}$ and the mobility decreased from $\sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $\sim 5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, possibly due to lower incorporation of Ga and poorer crystallinity UV-VIS spectra of the films exhibit sharp interference fringes, with high average transmittance of ~80 % in the visible region, limited by ~10-15 % average reflectance. All the conducting GZO films deposited with (4-5.5 %) O₂ in sputtering atmosphere at different substrate temperatures display a minimum in reflectance in the range of (1250–1800) nm due to plasma resonance, depends on the carrier concentration. These films exhibit optical band gaps in the range of (3.6–3.8) eV, which are significantly larger than ZnO bulk value (~3.3 eV). GZO films reveals a strong dependence of effective mass on carrier concentration, approaching a value of 0.7m₀ at carrier concentration of $\sim 10^{21} \text{ cm}^{-3}$. These features are attributed to high concentration of free carriers due to heavy doping, which are not observed in the films deposited with 6 % or higher O₂ in sputtering atmosphere. The increase in band gap is attributed to heavy doping effects, arising essentially from a combination of Moss-Burstein effect due to band filling and band gap shrinkage due to electron-electron exchange interaction.

PM07.09.12

Influence of Flash Lamp Annealing on Ga-Doped ZnO Films Rei Sugiura, Yasuji Yamada, Arisa Sakaguchi and Shuhei Funaki; Shimane University, Matsue, Japan.

Zinc oxide (ZnO) attracts many attentions to be studied as an oxide semiconductor. Resistivity of ZnO semiconductor added with Ga or Al is almost equal to Sn doped In₂O₃ (ITO). Recently, we have been studying electrical properties of Ga doped ZnO (GZO) films deposited by radio frequency (RF) magnetron sputtering at room temperature and revealed that annealing at high temperatures for 30 min improves electrical properties. As annealing temperature increases, mobility of GZO films were increases gradually. Carrier concentration increases as annealing temperature increases up to 350°C, however, it decreases at higher temperatures than 400°C. While longer annealing time reduces carrier density, shortening the annealing time in the order of a minute at a high temperature increases carrier density, resulting in electrical resistivity lower than the 350°C annealing for 30 min. From these behaviors of carrier density, we have concluded that the reduction of carrier density is caused due to zinc atom desorption from the GZO lattice. Therefore, it is very curious to know the effect of extremely short time annealing on carrier density and resistivity. Flash lamp annealing technique is used for very short time of annealing, as short as millisecond, often used in Si semiconductor industry. We applied this technique to the annealing of transparent GZO films as a post-annealing. GZO films with thickness of 200 nm were deposited on quartz glass substrates at room temperature by RF magnetron sputtering. These films were annealed by using a xenon lamp with the exposure pulse width from 1 to 5 milliseconds in the ambient atmosphere. Electrical properties and crystallinity were measured by van-der-Pauw method and XRD measurement. By the flash lamp annealing in appropriate pulse width and power, carrier density of the films increased and mobility was unchanged, resulting in decrease of resistivity. The change of properties of the GZO film by flash lamp annealing is different from conventional furnace annealing. The carrier density of GZO film decreases at higher temperatures than 400°C by a conventional furnace. On the other hand, it does not decrease by the flash lamp annealing as the power increases until the films are caused fatal damage. In conclusion, flash lamp annealing is effective to increase carrier density. However, due to less enhancement of mobility, resistivity of the films annealed for extremely short time is slightly higher than those annealed for typical annealing time using conventional heating equipment.

PM07.09.13

Structural and Mechanical Characterization of Amorphous Carbon-Silica Thin Films Deposited on Stainless Steel Substrates by PECVD Neileth J. Stand Figueroa¹, Erika Abigail Ochoa Becerra¹, Leonardo Mathias Leidens², Carlos Alejandro Figueroa², Fernando Lazaro Freire Jr¹ and Marcelo Eduardo Huguenin Maia da Costa¹; ¹Physics, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil; ²Universidade de Caxias do Sul, Caxias do sul, Brazil.

Nowadays, various materials are being studied, for instance, diamond like carbon (DLC) which has properties such as low friction coefficient, high hardness, mechanical wear resistance, optical transparency and high electrical resistivity, these properties can be modified used other elements such as Si, N, O, etc. The DLC thin film is very useful as a protective coating on metallic pieces such as stainless steel, but there is an issue: the low adhesion of the DLC on this type of substrate, caused by its high internal stress and low thermal stability. Our work is about the study an amorphous carbon-silica thin films used an organosilicon, this precursor was deposited using a rf-PECVD (radio frequency plasma enhanced chemical vapor deposition) on steel surface (ISO316L). The precursor was hexamethyldisiloxane (HMDSO) in its liquid state at room

temperature and atmospheric pressure.

Those films were deposited in several self-bias and two different substrate temperatures (200°C, 300°C, at room temperature there was no deposition). The deposition pressure was 2.6 Pa and they were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, profilometer measurements and nanoindentation.

Our results indicate that the temperature plays an important role in the adhesion of the amorphous carbon-silica thin film with the steel surface, although at temperatures lower than 150°C the adhesion is poor. The films deposited at 200°C and 300°C with different self-bias had an excellent adhesion, the spectra Raman showed that these films are amorphous and with X-ray photoelectron spectroscopy we noticed, that the percentage of Si-C and C-C binding increase as the self-bias. The hardness of these films were of the order of 20GPa.

PM07.09.14

Role of Organosilicon Films Deposited by PECVD Protecting Polypropylene Against Photodegradation Walter R. Waldman¹, Amanda d. de Freitas¹, Felipe Fernandes², Elidiane C. Rangel², Nilson C. Cruz², Adriana O. Silva¹ and Joyce Araujo³; ¹Federal University of São Carlos, Sorocaba, Brazil; ²University of São Paulo State-UNESP, Sorocaba, Brazil; ³Materials Metrology Division, National Institute of Metrology, Quality and Technology, Duque de Caxias, Brazil.

The sensitivity of polymers to photodegradation when exposed to the weather limits their options for outdoor use and reduces their shelf life. The deposition of thin films of organosilicon by plasma on polymers can influence its resistance to photodegradation without interfering in aspects such as color or brightness in bulk properties due to the transparency and nanometric dimension of these films.

Polypropylene samples were coated with organosilicon films by plasma-enhanced chemical vapor deposition (PECVD). First, a five-minute pre-treatment with oxygen gas, pressure 9 Pa, radiofrequency 13.56 MHz and power of 50 W. Subsequently the organosilicon films were deposited for 30 or 60 minutes at a pressure of 6 Pa, an atmosphere of 50 % of O₂ and 50% of HMDSO, radio frequency 13.56 MHz and power 80W. We exposed the samples to a UV-C light of fluorescent, germicidal, 15W power, maximum emission at 254 nm wavelengths, at 48, 96, 144 and 192 hours. We characterized the samples by MEV, FTIR, UV-Vis, XPS, profilometry and contact angle goniometry.

Films were homogeneous and continuous with a thickness between 300 and 550 nm and roughness between 20 and 30 nm. FTIR and XPS measurements after degradation showed that there was no difference between pure polypropylene and polypropylene coated with organosilicon films in the formation of indicators for polypropylene photodegradation, such as hydroxyls and carbonyls. It is clear that the organosilicon film did not offer photoprotection against the auto-oxidation cycle, so we expected the decrease of molar mass by the chain scission, consequent increase of the surface crystalline domains and formation of cracks, which compromise the mechanical properties making the material fragile. However, Scanning Electron Microscopy (SEM) results show that while fissures of virgin polypropylene have a width of 3.5 to 5 micrometers and a length of several millimeters, the polypropylene coated with organosilicon films had cracks with a width of 0.5 to 1 micrometer and length of 2 to 5 micrometers. Along to the fact that the organosilicon film keeps adhered to polypropylene during the photodegradation period, we conclude that the organosilicon film mechanically held the surface cohesion of the polymer material, limiting the crack propagation, despite the oxidation reactions of the polymer. This is, to our knowledge, the first observation of mechanical stabilization of polymers by thin films deposited in plasma. This role of the organosilicon thin film deposited on polypropylene can allow the development of protections for polymers exposed to the weather with benefits as the increase of the useful life and a smaller detachment of photodegraded layers, diminishing the environmental impact by the minor production of secondary microplastics.

PM07.09.16

Plasma Surface Treatment as an Important Tool for Polymers Applications Pericles L. Santana, José Roberto R. Bortoleto, Elidiane C. Rangel, Nilson C. Cruz and Steven F. Durrant; State University of Sao Paulo, Sorocaba, Brazil.

We demonstrated in this work, the use of plasma immersion techniques as an important tool for polymer surface modification. The treated polymers found out a lot of applications, one it is possible to change a thin layer of its surface keeping the bulk properties. Among the properties changed by plasma immersion techniques, it was analyzed the wetting on deionized water by contact angle measurements, surface morphology evaluated by Atomic Force Microscopy, the transparency at visible range using a UV-Visible-near Infrared Spectrometry and the barrier properties against water vapor measured by gravimetric method. The major results shows a selective surface physico-chemical properties being possible to obtain, hydrophobic or hydrophilic behavior, appearing smooth or rough surfaces, increase or loss of transmitted light, presenting an increase of barrier properties, depending on the plasma composition and technique used, when the temperature can be controlled during the processes. The quantitative measurements exhibit low or high values of contact angle, (Wettability), Surface roughness (Morphology), and Optical transmittance (Transparency) in the visible range. In most cases, the increase of barrier properties measured by gravimetric method is important for food packaging applications and optical devices, for example. Other applications can be considered for the treated polymers such as: biocompatibility, adhesion and medical applications.

PM07.09.17

Ammonia (NH₃) Gas Detection Based on Tin-Nitride Chemi-Resistive Sensor Teena Jangid and G. M. Rao; Indian Institute of Science, Bangalore, India.

Tin-nitride has not received the experimental attention given to similar IV-Nitrides such as Si₃N₄ and Ge₃N₄. Although Sn nitride has semiconducting properties, suitable for micro-electronic and optoelectrical devices, large disparity in the atomic radii of N and Sn poses a challenge in obtaining good quality tin-nitride films. In this study tin-nitride thin films were prepared on glass and Si substrates, by reactive radio frequency magnetron sputtering of metallic tin target (3" diameter and 3 mm thick) in nitrogen gas ambient. Process parameters such as substrate temperature, target-substrate distance, N₂ gas pressure and RF power were varied in a systematic way, to find-out best suitable combination of these parameters for growth of pure polycrystalline tin-nitride films. Deposited films were characterized for their crystalline structure and surface morphology by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) and results revealed that pure tin-nitride films can be grown at 600° C substrate temperature, 15 W RF power in pure nitrogen gas ambient, if target-substrate distance is fixed at 10 Cm.

To date, no work has been carried out on gas sensors, using tin-nitride as the sensing material for NH₃ gas. Chemi-resistive gas sensing characteristics of tin-nitride film (~60 nm thickness) deposited at optimized process parameters, were investigated for NH₃ in air at room temperature, as a function of gas concentration (10-70 ppm). Upon exposure to NH₃, the electrical resistance of the tin-nitride film was found to decrease. The sensor exhibited low base line drift and high sensitivity to NH₃ gas at concentrations as low as 10 ppm with fast response and recovery time at lower concentrations. The sensor exhibited a sensitivity of 0.065 (at 10 ppm) to 0.3 (at 70 ppm), t_{response} of 4 sec (at 10 ppm) to 23 sec (at 70 ppm), and t_{recovery} of 6 sec (at 10 ppm) to 23 sec (at 70 ppm). The NH₃ sensing mechanism can be explained on the basis of the depletion of chemisorbed oxygen at the film surface.

PM07.09.18

Dielectric and Ferroelectric Behaviors of Modified PZT Thin Films Synthesized by Pulse Laser Deposition Mohan K. Bhattarai¹, Alvaro Instan¹, Sita Dugu¹, Pawan Kumar^{1,2} and Ram Katiyar¹; ¹Physics, University of Puerto Rico, Rio Piedras, San Juan, Puerto Rico, United States; ²Physics, Gurukul Kangri University, Haridwar, India.

We synthesized highly oriented $0.90[\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})]0.10[\text{La}_x\text{Sc}_{1-x}]\text{O}_{3-\delta}$, where $0 \leq x \leq 0.6$ thin films on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) coated MgO (100) substrates utilizing laser ablation process in oxygen atmosphere. We optimized thin films deposited at a substrate temperature of 650°C using KrF excimer laser of wavelength, $\lambda = 248$ nm, $f = 5$ Hz and energy/pulse 270 mJ, and annealed at 700°C for half an hour in an oxygen atmosphere. The orientation of the thin films was examined by x-ray diffractometry. We carried out elemental analysis of thin films by high resolution X-ray photoemission spectroscopy (XPS). The morphology and surface roughness of thin films were analyzed by Atomic force microscopy (AFM). The dielectric measurements were conducted on LSMO/PLZTS/Pt metal-ferroelectric-metal capacitors using impedance analyzer as a function of temperature (100-600 K) and frequency (10^2 - 10^6 Hz). The ferroelectricity of thin films was probed by hysteresis measurements. High dielectric constant, low losses and high remnant polarization of thin film capacitors are suitable characteristics for applications in electronic devices.

PM07.09.19

In Situ Stress Measurements of W and Nanocrystalline Nanotwinned Cu Deposited by HiPIMS [Alison Engwall](#), Swanee J. Shin and Yinmin Wang; Lawrence Livermore National Laboratory, Livermore, California, United States.

High power impulse magnetron sputtering (HiPIMS) is an emerging method for the deposition of thin films. Pulsed power applied to a sputtering target at a low duty cycle and high power density generates a dense plasma with a high percentage of sputtered ions. The resulting films have improved properties of adhesion, hardness, density, and uniformity compared to films deposited with traditional magnetron sputtering. The technique also shows potential in synthesizing advanced microstructures such as nanocrystalline nanotwinned films. In-situ stress measurements have been performed on HiPIMS W and nanocrystalline nanotwinned Cu and contrasted with DC sputtered films under similar processing conditions, followed by characterization and microstructure analysis of the resulting films.

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PM07.09.20

Laser Ablation of Molybdenum foil Immersed in Precursor Solution [Mustafa Mozael](#), Bernard Kear and Stephen D. Tse; Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States.

Titanium dioxide belongs to the transition-metal oxide family and forms several polymorphs, including anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). In comparison with other polymorphs, anatase- TiO_2 is preferable for solar cell applications because of its high electron mobility, low dielectric constant, and low density. The main drawback is that it does not absorb well visible light. In this work, a novel method is used to synthesize amorphous molybdenum-doped- TiO_2 nanoparticles, which upon subsequent post-annealing, transform into nanocrystalline structures. The resulting nanoparticles display photocatalytic activity, which is improved after doping, in comparison to that for un-doped nanoparticles. Amorphous Mo-doped- TiO_2 nanoparticles are synthesized using pulsed-laser decomposition of a molybdenum foil immersed in liquid titanium tetraisopropoxide (TTIP). Interaction between the focused laser beam and the Mo substrate generates a submerged-plasma, where vaporization of the Mo substrate along with decomposition of the liquid precursor combine to produce Mo-doped TiO_2 nanoparticles upon quenching by the surrounding unreacted liquid precursor. The as-synthesized nanoparticles have non-crystalline or amorphous structures, primarily because of rapid condensation and quenching of vaporized species from the plasma-reaction zone. Interestingly, upon subsequent heat treatment in air or oxygen, starting at $\sim 400^\circ\text{C}$, transformation to the more stable anatase- TiO_2 phase occurs, but doped with molybdenum. Initial results show that Mo-doped anatase TiO_2 exhibits a higher UV and visible photochemical activity than that for un-doped anatase- TiO_2 . Heat treating the nanopowders were investigated in this work to study the effect on crystal structure of TiO_2 after doping with molybdenum ions. It is notable that the phase transformation from anatase to rutile of Mo-doped TiO_2 samples is delayed a certain temperatures, implying that the molybdenum may help to stabilize the anatase phase.

PM07.09.21

Micro-Plasma Based Enhancement in Dielectric and Piezoelectric Properties of ZnO and BaTiO₃ Based Multifunctional Composite Thin Films by Surface Modification—Comparison of Plasma Regimes and Materials Characterization Using Corona Discharge [Harlavpreet Brar](#)¹, Walker Tuff¹, Saquib Ahmed², Ebertho Leal-Quiros³ and Sankha Banerjee¹; ¹California State University, Fresno, Fresno, California, United States; ²Mechanical Engineering, Buffalo State College, Buffalo, New York, United States; ³Mechanical Engineering, University of California, Merced, Merced, California, United States.

Atmospheric pressure and ambient temperature based micro-plasmas have been used in polarization and alignment of dipoles in ferroelectrics. The same phenomenon can be used to enhance the surface energy and surface characteristics of composite multifunctional thin films by means of surface modification. The current work involves the use of dielectric barrier and corona discharge based atmospheric micro-plasmas to treat ZnO-Epoxy-BaTiO₃ nano-composite flexible thin films towards enhancement in electrical, dielectric and piezoelectric properties of these composites. The ZnO volume fraction is varied from 1-10%, while the BaTiO₃ volume fraction is held constant at 40%. Both voltage driven (stable) and current driven (pulsed) corona discharge regimes are identified and used to process the thin films. The voltages in the stable regimes are varied from 8 – 11 kV, while the current is held constant around 0.01 mA. The current in the pulsed regime is varied from 0.05 – 0.1 mA and the voltage is held constant around 9 kV. The surface properties are characterized by multi-point probe measurements to map and analyze the effect of the different plasma regimes. The composite thin films are also tested for their bulk dielectric, impedance, electrical and piezoelectric properties. The effects of the different plasma regimes on the surface micro-structure are analyzed using a scanning electron micrographs and energy-dispersive x-ray spectroscopy.

PM07.09.22

Synthesis of Nanoscale Optical Multilayer Coatings via Reactive Magnetron Sputtering [Chelsea D. Appleget](#) and Andrea Hodge; Aerospace and Mechanical Engineering Department, University of Southern California, Los Angeles, California, United States.

Optical multilayers are comprised of nanoscale layers, where the layers are arranged to alter the way the material reflects and transmits light. The interplay of these nanolayers increases the potential for novel combinations of properties, including transparency and strength. These characteristics are important for applications that require light penetration for function but a robust barrier for protection. For these reasons, optically transparent multilayers are promising materials because they offer extraordinary strength, hardness, heat resistance, and most importantly, transparency in both the UV/Vis/NIR wavelengths.

A series of optical nanomultilayers were synthesized using sequential DC and RF reactive magnetron sputtering. The nanomultilayers were designed using predictive methods for maximized optical transmittance, and the experimental results were compared with calculated transmittance values. The effects of deposition parameters were examined in order to understand their influence on the interface, microstructure, mechanical deformation and light propagation of the films. As-sputtered layer roughness, interfaces, and texture were characterized using SEM, TEM, and XRD. Overall, this work focuses on reactive

magnetron sputtering of multifunctional nanoscale multilayers, and the effect of the as-deposited microstructure on resulting mechanical and optical properties is discussed.

PM07.09.23

Iron Oxide-Hydroxide Photovoltaic Nanomaterials Synthesized by Atmospheric Micro-Plasma Aysha Shamaki¹, Marieme Ndaw¹, Sz-Chian Liou², Sabin Pokharel¹, Mobolaji Zondode¹, Saroj Pramanik³, Jiang Li⁴, Abdellah Lisfi¹, Yongle Pan⁵ and Yucheng Lan¹; ¹Department of Physics and Engineering Physics, Morgan State University, Baltimore, Maryland, United States; ²Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ³Department of Biology, Morgan State University, Baltimore, Maryland, United States; ⁴Department of Civil Engineering, Morgan State University, Baltimore, Maryland, United States; ⁵U. S. Army Research Laboratory, Adelphi, Maryland, United States.

With the increasing global energy demand and diminishing fossil fuel reservation, renewable and environmental-friendly sustainable energy is interested in the past years. Solar photovoltaic technology is a promising way to collect solar energy into electricity directly. Iron hydroxides are one kind of candidate materials for photovoltaic materials because of their abundance on earth and chemical stability in aqueous media. Here, iron oxide-hydroxide was synthesized in aqueous solutions by the atmospheric micro-plasma. The hydroxide powders were characterized by X-ray powder diffraction, transmission electron microscopy, Raman scattering, and UV-vis spectroscopy. The effects of pH values, electric fields, and synthesis temperatures etc, were systematically studied on morphology, crystallinity, magnetic property, band-gap, and UV-visible light absorptions. The plasma reaction mechanism was discussed. The as-synthesized nanomaterials were further fabricated into dye-sensitized solar cells and their photovoltaic properties were investigated.

PM07.09.24

Controllable Plasma Based Synthesis of MoS₂ for Optoelectronic Applications Dipanjan Nandi¹, Dhanvini Gudi¹, Xinsong Lin², Andrea Sedgwick², Manisha Gupta¹ and Jiixin Fan³; ¹Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada; ²Centre for Oil Sands Sustainability, Northern Alberta Institute of Technology, Edmonton, Alberta, Canada; ³Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Recent advancement of two dimensional (2D) materials paves new avenues for potential optoelectronic and nanotechnology applications. Advancement in molecular biology, atomic and molecular physics demands new techniques to explore the atomic level features of different 2D materials as these materials have exciting optoelectronic properties [1, 2]. Mechanical exfoliation and chemical vapor deposition (CVD) are two well-known techniques for MoS₂ synthesis. Monolayers of MoS₂ are attached with van der Waals forces and can hence be exfoliated easily. However, it is difficult to control the structural parameters such as size, shape, and thickness of the exfoliated MoS₂ flakes. CVD technique used for synthesis of good quality MoS₂ crystals lacks in *in-situ* thickness control. Pulsed laser deposition (PLD) is a well-established laser plasma based material growth technique to maintain good stoichiometry for complex compound materials with good control in thickness and repeatability.

In this work, PLD technique is used for growing large area homogenous MoS₂ thin films for nanoscale optoelectronic applications. This study focuses on the optimization of the PLD growth parameters for obtaining high-quality uniform large area MoS₂ thin films on quartz, sapphire and SiO₂/Si substrates and characterizing the physical properties. In this work, a pulsed KrF (248 nm, 15 ns, 10 Hz) laser is used for ablation of the 99.9% pure MoS₂ target. Major parameters influencing the quality of MoS₂ thin film like the laser fluence, target-substrate distance, substrate material and temperature along with the ambient gas pressure will be optimized to obtain thin films with high crystallinity and mobility.

Initial growths at different temperatures (room temperature to 850°C) indicate higher crystallinity at higher temperatures like 700°C to 850°C. Also, we have been able to control the growth time to obtain 2-3 monolayer MoS₂ thin films, which have been confirmed by the Raman peaks at 382.1 cm⁻¹ and 404.9 cm⁻¹. Initial measurement at room temperature shows electron mobility of 0.19 cm²/V-s for ~30 monolayers. Metal-oxide-semiconductor capacitor will be fabricated to calculate the doping concentrations and Hall measurements will be performed to calculate the carrier mobility. Material, optical and electrical characterization of the optimized MoS₂ thin films grown using PLD will be presented. Future prospects of this work is to fabricate nanoscale field effect transistors on flexible substrates for flexible electronic applications.

Reference:

1. Yan Chen *et al.*, *ACS Appl. Mater. Interfaces*, 8, 47, 32083-32088 (2016).
2. Woong Choi *et al.*, *Advanced Materials*, 24, 43, (2012).

PM07.09.25

Plasma Synthesis of AlNiCo Core/Shell Nanopowders Ayse M. Genc, Tayfur Ozturk and Yunus E. Kalay; Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey.

Aluminum-nickel-cobalt (AlNiCo) permanent magnets revolutionized the permanent magnet industry in 1920's but has not been thoroughly studied after the development of powerful rare-earth permanent magnets. As compared to rare-earth magnets, AlNiCo magnets have high remanent force (Br), better corrosion resistance and higher Curie temperature but lack high coercivity. If the coercivity is improved, BHmax value may increase up to values that would potentially fill the gap in between rare-earth and rare-earth free permanent magnets. The alloy stands as a good candidate to be produced with novel methods and investigated with the latest analysis techniques and it is now well established that magnetic behavior is strongly dependent on the size of the nanoparticles. In this work, magnetic properties of micron-size ball-milled powders and radio frequency (RF) plasma synthesized core-shell nanoparticles are compared. Scanning transmission electron microscopy (S/TEM) analysis of the plasma synthesized nanoparticles showed a core/shell structure in which AlNiCo powders were encapsulated with magnetic Fe₃O₄. The magnetic measurements indicated that coercivity increased significantly with decreasing particle size, particularly for the nanoparticles encapsulated with hematite (Fe₃O₄) layer. It is likely that this oxide coating contributes to the increase in coercivity due to effective exchange coupling between the core and the shell structure while serving as a protective layer against room temperature oxidation. The magnetic behavior of AlNiCo powders with respect to size and core-shell structure formation will be discussed in details in conjunction with TEM, S/TEM, VSM and XRD results.

Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 107

8:30 AM *PM07.10.01

Metal Nanoparticle/Nanocarbon Hybrid Nanostructures Synthesized via Plasma-Liquid Interaction and Their Potential Applications in Biomedical Field Dan Sun¹, Daye Sun¹, Brian Falzon¹, James McLaughlan^{3,4} and Paul Maguire²; ¹Queen's University Belfast, Belfast, United Kingdom; ²Ulster University, Newtownabbey, United Kingdom; ³School of Electronic and Electrical Engineering, University of Leeds, Leeds, United Kingdom; ⁴Leeds Institute of Cancer and Pathology, University of Leeds, Leeds, United Kingdom.

Non-equilibrium atmospheric pressure plasma has emerged as a new platform technology for the synthesis/surface engineering of various nanomaterials. When interacting with water, a high density of gas phase plasma electrons become solvated in the liquid, creating a rapid cascade of transient non-linear chemical reactions and highly reactive radicals. As plasma induced species and reactions propagate through the liquid, they are interrupted at solid surfaces, leading to energetic final reactions. In this work, we deployed a direct current (DC) room temperature atmospheric pressure plasma (APP) for the in situ synthesis of gold nanoparticle /nanocarbon (AuNP/NC) hybrid structures in aqueous solutions. More specifically, carboxyl functionalized multi-wall carbon nanotubes and graphene oxide nanosheets have been decorated with different sized AuNPs through manipulating the gold salt (HAuCl₄) precursor concentration in the aqueous mixture. UV-vis spectroscopy and zeta potential analysis suggested that the bonding between the [AuCl₄]⁻ complex and nanocarbons carboxyl functional group took place prior to the APP processing. These binding sites facilitated the preferential nucleation and growth of AuNPs through the APP induced liquid chemistry. The AuNP/nanocarbon hybrids also demonstrate enhanced Raman scattering and greater photothermal conversion efficiency under the irradiation of NIR laser, hence may hold great potential in future multi-modal cancer treatment involving bio-imaging and hyperthermia therapy.

9:00 AM PM07.10.02

Antimony-Doped Tin Oxide Nanocrystals Synthesized by Low Temperature Plasma Qinyi Chen and Elijah Thimsen; Washington University in St. Louis, St Louis, Missouri, United States.

For electrochemical applications, metal-oxide materials have attracted research interest as alternative electrode materials for reactions occurring at positive potentials in the presence of water.¹ Often, these metal-oxide materials function as an electrically-conductive support for a noble metal catalyst, and therefore must have very high specific surface area and uniform distribution of the particles. Among thermodynamically stable metal-oxide materials, antimony-doped tin oxide (ATO) stands out with its combination of: 1) high electrical conductivity by incorporation of suitable Sb doping, 2) high chemical stability over a wide range of pH values and reduction potentials, and 3) abundant constituent elements. In liquid phase, sol-gel and colloidal methods are widely used to synthesize ATO nanocrystals. However, to meet the electronic conductivity requirements, post-synthesis anneal treatments are required to activate the electron donors and increase the conductivity of ATO nanocrystal assemblies prepared using liquid-phase techniques, which may adversely affect the surface area and size distribution of the material. In this work, we report on our efforts to synthesize monodispersed, conductive ATO nanocrystals through a single-step low temperature plasma growth method without any post treatments. Precursor vapors of tin and antimony were fed into a radiofrequency, flow-through low temperature plasma reactor. ATO nanocrystals were formed in plasma by reacted precursor vapors. Thin films comprised of ATO nanocrystals were then immediately deposited by inertial impact deposition of the aerosol resulting from plasma synthesis. A variety of methods were utilized to characterize the resulting materials, and determine properties such as film thickness, porosity, nanocrystal size, and elemental composition. Local electron concentration and mobility within the nanocrystals were investigated by Fourier-transform infrared (FTIR) absorption spectroscopy. Hall effect was used to characterize longitudinal electrical transport in the thin film. The nanocrystal growth mechanism in the plasma will be discussed with a focus on antimony dopant incorporation, and the effects of nanocrystal size on the transport properties of ATO thin films will be presented in this work.

1 Dubau, L. *et al.* A review of PEM fuel cell durability: materials degradation, local heterogeneities of aging and possible mitigation strategies. *Wiley Interdisciplinary Reviews: Energy and Environment* **3**, 540-560 (2014).

9:15 AM PM07.10.03

Directed Plasma Synthesis of TiO₂ Nanopatterning for Templated Growth and Alignment of Au and Alloyed Nanoparticles Ming Kit Cheng, Brandon J. Holybee, Akshath R. Shetty and Jean Paul Allain; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

TiO₂ has been an important semiconductor for optical applications including: photovoltaics and photocatalysis, due to favorable properties such as wide band gap, chemical stability and low cost. Recently the incorporation of photonic crystal (PC) structures and noble metal nanoparticles (NPs) on the free surface have been carried out to exploit the photonic and plasmonic resonance in enhancing absorption of a broader sunlight spectrum. The optical performance can be further improved if they can be coupled. A versatile processing synthesis approach that can control the shape, size and alignment of NPs to scale is needed to maximize the coupling. Directed low-energy plasma and ion-beam synthesis is a promising technique to induce complex nanopatterns such as ripples on various material surfaces. These nanopatterns can then act as a template for the growth and alignment of NPs with high areal density at nanometer scales. Ions extracted from plasma can also modify the surface chemistry and wettability, which mediates NP growth kinetics and adhesion onto the surface. However, few research focuses on plasma-based nanosynthesis on TiO₂ despite its wide usage, unlike other widely-used materials such as Si. Therefore, it is necessary to first examine the parameters necessary to nanopattern TiO₂ via plasma nanosynthesis. Moreover, when dealing with a non-flat surface with PC structures, additional factors such as non-uniform sputtering rate across the surface and shadowing effects by the structures have to be examined.

We were able to induce periodic ripples with wavelength and amplitude varying between 14-57 nm and 0.9-3.0 nm respectively on a 100 nm thick TiO₂ film coated on a polymer substrate with 1D diffraction gratings via Ar⁺ and O₂⁺ irradiation at an oblique angle and varying fluence. The photonic resonance peak of the substrate was blue-shifted from 860 nm to as low as 838 nm. In a particular case in which the beam orientation is oblique relative to the gratings, an additional peak about 40 nm higher than the primary one appeared. Moreover, while both Ar⁺ and O₂⁺ can nanopattern TiO₂, Ar⁺ created oxygen vacancies and reduced the oxide while O₂⁺ suppressed its formation. Ordered ripples also appeared at a lower fluence with less defects when using O₂⁺. Our goal is to utilize these ripples for a templated NP growth by glancing angle PVD, by exploiting the shadowing effect by the ripples to facilitate nucleation and NP alignment. We will investigate the ability to tune the NP size, shape and spacing and its plasmonic properties by varying the ripple dimensions and deposition parameters, in order to achieve broadband absorption and coupling with photonic resonance. We will also examine whether creating or suppressing oxygen vacancies is more beneficial to NP growth. For the composition of the NPs, we will not only examine conventional Au NPs, but also novel metallic alloy NPs that is cheaper, more sustainable and absorbs light more efficiently.

9:30 AM PM07.10.04

Nanocomposite Thin Films Obtained with Cold Atmospheric Pressure Plasma Processes Jacopo Profili and Luc Stafford; Université de Montréal,

Montreal, Quebec, Canada.

In the last decade, many efforts have been made for the understanding and the analysis of nanocomposite thin films. The new properties created by these materials open a wide range of possibilities for new industrial applications. Different physical and chemical advanced processes are used to develop these products. Among them, low plasma pressure processes have been studied since Philips's work in 1982. Today, the desire to reduce production costs and environmental impacts of the manufacturing process allowed the study of new plasma approaches at atmospheric pressure. These systems offer the possibility to reduce the amount of precursor and favor the process scale-up in a production line. Recently, some researchers have demonstrated the possibility to use colloidal suspensions as precursors for the synthesis of nanocomposite thin films in atmospheric pressure dielectric barrier discharge (DBD). This approach broadens the chemical range of obtainable nanocomposites because of the large variety of commercially available suspensions. Through this work, we aim to highlight the current understanding of the process and the remaining scientific challenges for the synthesis of a homogeneous distribution of chemical phases with plasma treatment. The DBD is obtained between two parallel alumina plates separated with 1 mm gas gap. An AC high voltage in the kHz frequency range is used to sustain a homogeneous Townsend discharge in N₂-N₂O gas mixtures. Titanium dioxide nanoparticles (TiO₂ NPs, anatase phase, 20 nm in diameter) are functionalized and mixed with Hexamethyldisiloxane (HMDSO) to get a stable colloidal solution. This suspension is injected in the gas mixture using a pneumatic injector coupled to a nebulizer. The obtained colloidal aerosol is then evaporated before reaching the discharge chamber. Plasma-deposited coatings were then characterized by SEM, FTIR and XPS. The hydrodynamic radius of particles (and agglomerates) in the colloidal solution was determined using Dynamic Light Scattering analysis (DLS). The electrical analysis of the process shows that the discharge remains stable and homogeneous during the injection of the suspension, indicating that nanoparticles do not affect the physical regime of the discharge. The SEM analysis indicates that spherical agglomerates remain included in a dense matrix or stuck on the surface. The size distribution of these structures can be larger than 1 micrometer, *i.e.* bigger than the coating thickness. The Raman peak at 143 cm⁻¹, associated with the anatase structure, shows no structural change of NPs during their interaction with the discharge. Our results show that the observed agglomeration can take place at different steps of the process, including in the initial suspension, during the atomization process and as a result of plasma interactions. Finally, our results reveal that the transport dynamics of NPs can judiciously be controlled using custom-designed voltage waveform.

9:45 AM PM07.10.05

Additive Manufacturing of Nanomaterials Using Plasmas Kyle O'Shea, [Alexander Ho](#) and Rebecca J. Anthony; Michigan State University, East Lansing, Michigan, United States.

Plasma reactors have been used for synthesis of many types of nanomaterials with great success, from a range of materials including semiconductors and metals. These reactors feature versatile operation across pressure, power, and size regimes. While low-pressure plasmas typically lead to nanoparticle ensembles with the narrowest size distributions, atmospheric pressure plasmas can produce high-quality and tunable nanocrystals particularly when the reactor size is miniaturized. Both the small reactor size and atmospheric pressure operation contribute to the potential to use these reactors in roll-to-roll manufacturing and other large-scale deposition schemes, removing batch post-processing steps and enhancing the ability to incorporate the nanoparticles into the manufacturing stream.

Here we present our work on additive manufacturing of silicon nanoparticles using an atmospheric pressure glow discharge. The reactor consists of a quartz tube encircled by a powered coil electrode (one end floating) supplied with RF power at 13.56 MHz, together with a coaxial central ground electrode. We supply silane and argon gas (total gas flowrate ~ 200 sccm) for silicon nanoparticle production. Silicon nanoparticles are produced in the plasma and spray out of the tube onto the substrate beneath. The nanoparticles are crystalline with a relatively wide size distribution (5-40nm) as verified using transmission electron microscopy and the ensembles exhibit photoluminescence near 600 nm. The reaction is performed in air, and the nanoparticle surfaces are coated in an oxynitride layer as determined using Fourier-transform infrared spectroscopy. The reactor is mounted to a computer-controlled 3D manipulator which allows the nanoparticles to be deposited in pre-programmed patterns in all three coordinates directly out of the reactor. Our current work focuses on characterizing the deposition properties including porosity, mechanical properties, and yield while simultaneously engineering the reactor to enable narrower linewidth and a smaller size distribution of nanoparticles, along with controlled shell composition and thickness using additional gas flows. This work could lead to directly printable nanocrystal layers and coatings for in-situ fabrication of devices and other technologies.

10:00 AM BREAK

SESSION PM07.11: Thin Films, Coatings and ALD II
Session Chairs: Tomohiro Nozaki and Dan Sun
Wednesday Morning, November 28, 2018
Hynes, Level 1, Room 107

10:30 AM *PM07.11.01

Nanosecond-Pulsed Cold Plasma in Liquid Nitrogen for the Synthesis of Nitrogen-Based Materials [Danil Dobrynin](#), Roman Rakhmanov and Alexander Fridman; Drexel University, Camden, New Jersey, United States.

The application of strong electric fields in water and organic liquids has been studied for many years, because of its importance in electrical transmission processes and its practical applications in biology, chemistry, and electrochemistry. More recently, liquid-phase electrical discharges have been investigated, and are being developed. Recent advances in pulsed power technology permitted application of much faster voltage rise times (including the subnanosecond range) and revealed that plasma-like phenomena can, in fact, occur in fluid phase quasi-homogeneously without any bubbles and voids. Very sharp rise times leads to overvoltage and development of a non-thermal discharge (direct ionization of liquid phase) before fluid moves forming bubbles or gas voids. Here we present the first results on characterization and diagnostics of nanosecond-pulsed discharge in liquid nitrogen and characterization of produced materials.

* This work is supported by the Army Research Office (grant # W911NF-17-1-0597, PI: Dobrynin).

11:00 AM PM07.11.02

Synthesis, Processing, and Characterization of Materials Processed by Spark Plasma Sintering [Kaya Wei](#)^{2,1} and George Nolas¹; ¹University of South Florida, Tampa, Florida, United States; ²National High Magnetic Field Laboratory, Tallahassee, Florida, United States.

Spark Plasma Sintering (SPS) has been employed as a very effective method for consolidation of powders into dense polycrystalline materials. We have employed SPS as a unique approach for material synthesis, including crystal growth. Moreover, due to the internal localized heating during SPS

processing, the rapid, low temperature densification of fine-grain powders can be realized. Since only the surface temperature of the sample powders rises rapidly by self-heating, grain growth is minimized, thus high density, bulk polycrystalline semiconductors with nano-scale grains can be achieved. This technique is important in obtaining thermoelectric materials whereby grain-boundary scattering is realized thus allowing for materials with enhanced thermoelectric performance, as compared to the same polycrystalline material with micro-scale grains. A variety of examples, including synthesis and, in particular, the crystal growth of materials with complex crystal structures that have not been previously synthesized even in microcrystalline form, will be presented. In addition, our consolidation technique for nanostructured materials will be discussed, with specific emphasis on an understanding of specific processing conditions and their effect on the morphology of different semiconductors and the resulting grain size and product density.

11:15 AM PM07.11.03

Effect of Zr Target Power on Structure Property Relations of Ni-Zr Alloy Thin Films Processed by DC Magnetron Co-Sputtering [Bibhu P. Sahu](#)^{2, 1}; ¹Indian Institute of Technology Kharagpur, Kharagpur, India; ²Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, India.

A comparative study has been carried out on microstructural evolution, surface roughness, nanoindentation and scratch behavior, electrical resistivity, and corrosion resistance of $\text{Ni}_{1-x}\text{Zr}_x$ ($0.13 \leq x \leq 0.40$) thin films deposited on Si-(100) substrate by DC magnetron co-sputtering of high purity elemental targets in argon atmosphere. The Zr target power has been changed from 75 watt to 175 watt by keeping the Ni power constant at 200 watt. The film compositions have been examined by energy dispersive X-ray. Grazing incidence X-ray diffraction (GIXRD) studies have shown presence of Ni-rich solid solution, Ni_3Zr and amorphous phase in all the films, with Ni_5Zr being additionally observed in the $\text{Ni}_{87}\text{Zr}_{13}$ film. Analysis of GIXRD data along with transmission electron microscopic studies have shown that volume fractions of both amorphous phase and Ni_3Zr are increased, whereas the average crystallite size is decreased with increase in Zr concentration. Nanoindentation hardness and Young's modulus as well as electrical resistivity measured by Van-der Pauw four-probe method are influenced by volume fractions of both Ni_3Zr and amorphous phase. Surface roughness and coefficient of friction obtained from atomic force microscopy and nano-scratch experiments, respectively decrease, whereas corrosion resistance in 3.5 wt% NaCl solution increase with Zr concentration primarily due to increase in amorphous phase content. Resistance to pitting corrosion is facilitated by formation of ZrO_2 -rich passive film, as confirmed by X-ray photoelectron spectroscopy.

11:30 AM *PM07.11.04

Atmospheric Pressure High Power Impulse Plasma Source (HiPIPS) for Deposition of Metallic Coatings [Vasiliki Poenitzsch](#) and Ronghua Wei; Southwest Research Institute, San Antonio, Texas, United States.

Southwest Research Institute (SwRI) is developing a novel atmospheric pressure, non-thermal High Power Impulse Plasma Source (HiPIPS) technique for field applicable deposition of metallic protective coatings. The HiPIPS technology is an advanced variation of atmospheric pressure plasma process that uses high power pulsed DC generators. Power is applied in microsecond pulses at low duty factor ($< 10\%$) and low frequency (≤ 1 kHz) leading to high peak power densities (tens of kWatts) and high peak currents (hundreds of Amps) of while keeping low overall power (< 50 W) and low processing temperatures (< 50 °C). These conditions result in the generation of a highly dense plasma discharge, with increased ionization for surface modification and deposition of coatings. SwRI has conducted a systematic experimental study on the HiPIPS process parameters and resultant coating properties towards proof-of-concept development of HiPIPS deposition of CoCr, Ti-6Al-4V and TiN coatings. Plasma properties were characterized using current-voltage probes and optical emission spectroscopy (OES). The microstructure and elemental composition of resulting deposited were examined using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD).