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Fabrication and characterization of spin-coated TiO_2 films

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Abstract

Porous TiO_2 films were deposited on glass and ITO coated glass substrates by spin coating for spinning rates of 2000, 5000, 2000 followed by successive run of 5000 rpm (2000-5000). The AFM, SEM, XRD and UV-Vis analysis of the films coated on bare glass substrates for individual and 2000-5000 rpm runs showed amorphous and crystalline behaviours respectively, while TiO_2 films deposited on ITO/Glass substrates show crystalline structure. Both substrate nature and thickness of the films influence the formation of the crystallinity of the films. Also AFM images reveal that the roughness values of the films are independent of substrate.

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Keywords: TiO_2 films; optical properties; electron microscopy; spin coating technique, XRD.

1. Introduction

Recently titanium dioxide is one of the vast studied metal oxides, which is so transparent, chemically stable, relatively hard and inexpensive. Titanium dioxide is a wide band gap semiconductor, which owing to its photo-conversion properties in the UV spectrum range shows various useful applications. Since TiO_2 films have three

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anatase, rutile, and brookite phases [1–4], it is used for different applications including optical cells [5], conversion of solar energy [6]. TiO_2 have been also used attractively as an n-type window layer in solar cells [7].

It is essential to choose the appropriate fabrication method for the film deposition, in order to get good optical and electrical properties. Different methods such as electron beam evaporation, sputtering, chemical vapour deposition, sol–gel process [8-11], have been used to prepare TiO_2 films. The spin coating sol–gel method is a low cost large surface area liquid-deposition process yielding homogeneous deposits [12,13], for which the properties of the films can be controlled by the solution composition. Spin coating process is composed of an adjustment of the spin speed and viscous centrifugal force.

In this study, using sol-gel spin coating method for different runs, highly porous TiO_2 films were deposited on two different glass and ITO coated glass substrates. Here parallel to the previous study three different runs of spin coated films were compared which two different single run time (2000 and 5000 rpm) films were compared to thick two successive run time (2000-5000) film. Thickness measurements, optical, electrical and morphological characterizations were conducted by SEM, AFM, UV-Vis spectrometer, BET and XRD techniques.

2. Experimental

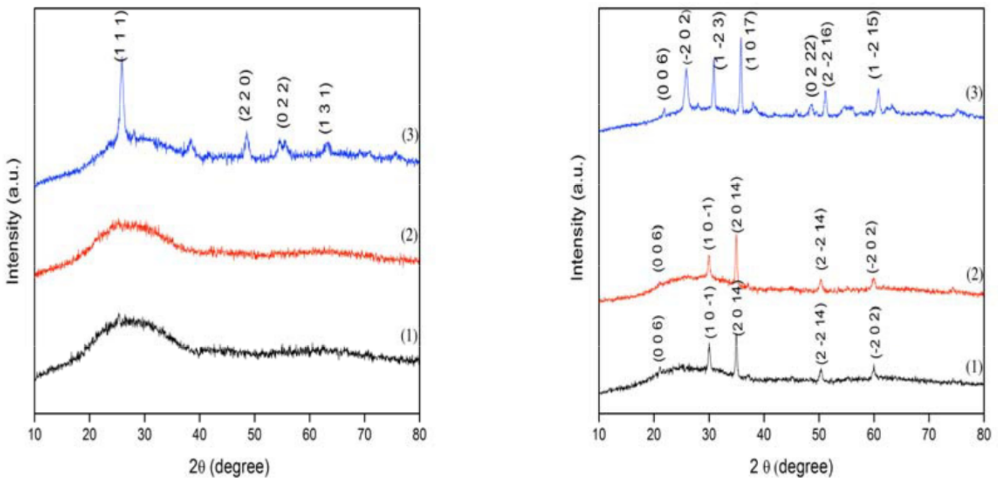
The sol-gel method was used to prepare TiO_2 solution, the procedure followed to prepare the nanoporous TiO_2 is given in the previous work [7]. This solution is used to prepare films of different thicknesses by spin coating method on both bare glass and ITO coated glass substrates at different speeds of 2000, 5000 and 2000-5000 rpm each for 1 min. The spinning for 2000-5000 was first made at 2000 rpm proceeded by 5000 rpm each for 30 sec. The films after drying at 120 ^{o}C for 5 min are subsequently heat-treated at 450 ^{0}C for 30 min in nitrogen flow.

The structure of the films were determined by X-ray diffraction (XRD) using the CuK_{α} radiation (154 nm) in the range 10°-80° (2θ). The cross sectional and surface morphology of the films were analysed using a FEI Quanta 400 FEG model Scanning Electron Microscope (SEM) following the depositions of thin (300Å) gold films, which were found to have different thicknesses for different runs. The study of optical transmission of the films was done by measuring the absorbance spectra of samples by LAMBDA 950 UV/Vis/NIR Spectrophotometer in the wavelength range 320–1050 nm. The AFM imaging was used to realize the surface topography of samples using a Veeco Multi Mode V AFM system. All these structural measurements were done at room temperature.

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of powder TiO_2 revealed polycrystalline structures. From the powder pattern, even negligible, small intensity of rutile peak is obtained as it was shown elsewhere [7]. XRD analysis of TiO_2 films coated on glass substrates for 2000 and 5000 rpm spinning rates showed that these films were amorphous, Whereas 2000-5000 rpm spin-coated film showed crystalline phase with preferred orientation along (111) plane and diffraction angle 2Θ~26°, that is shown in Figure 1. As it is observed from Figure 1, the XRD patterns of TiO_2 films deposited on ITO/Glass substrates all show crystalline structure, beside, increasing the coating speed for ITO/TiO_2 films improves the intensity of diffraction peaks. It is observed that both substrate nature and thickness are important factors to determine the crystalline or amorphous structure of the films. Crystallite sizes calculated from the XRD pattern using the Scherrer's formula [14,15] were found to be 24 nm, and 6.5 nm for powder and 2000-5000 films, respectively.



a) b)

Fig. 1. XRD patterns of TiO_2 films deposited on a) glass substrates b) ITO coated glass substrates, using spin-coating speeds of (1) 2000, (2) 5000 and (3) (2000-5000) rpm

3.2. Scanning electron microscopy

Figure 2 shows SEM images of spin-coated TiO_2 films. The films contain pores and particle sizes about 50-100 and 20 nm respectively, which are in consistent with X-ray measurements. So the most important factor of having high surface area of the films for nano-crystalline solar cell material structure is provided. According to the SEM cross-sectional images the films thicknesses are dependent on the spin rate. The films have no visible agglomeration on the surface indicating the proper homogenization of the used pastes.

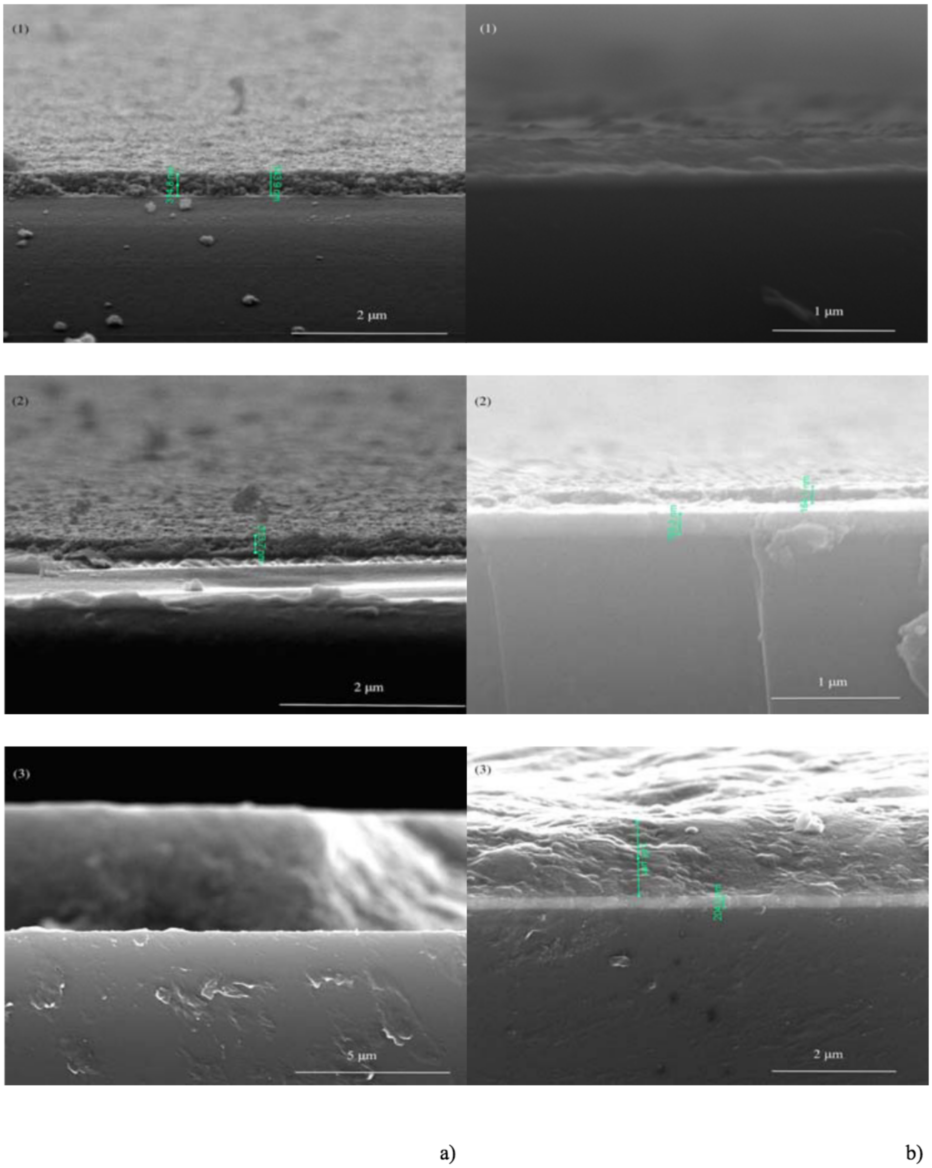


Fig. 2. SEM micrographs of TiO_2 films deposited on a) glass substrates b) ITO coated glass substrates, using spin coating speeds of (1) 2000, (2) 5000 and (3) (2000-5000) rpm

3.3. Atomic force microscopy

The AFM images (Figure 3) show that films are porous with pore size of about 50-100 nm. Table 1 shows that there is no obvious dependency of roughness value to the spinning rates. It can be seen that the deposited films are rougher for ITO substrates compared to glass substrates for 2000 and 5000 rpm spinning rates. Beside for (2000-

5000) rpm spinning rate any difference between roughness values of both substrates were observed. The high roughness value which means higher active surface, is a favourable material property to be used as the substrate layer of the device.

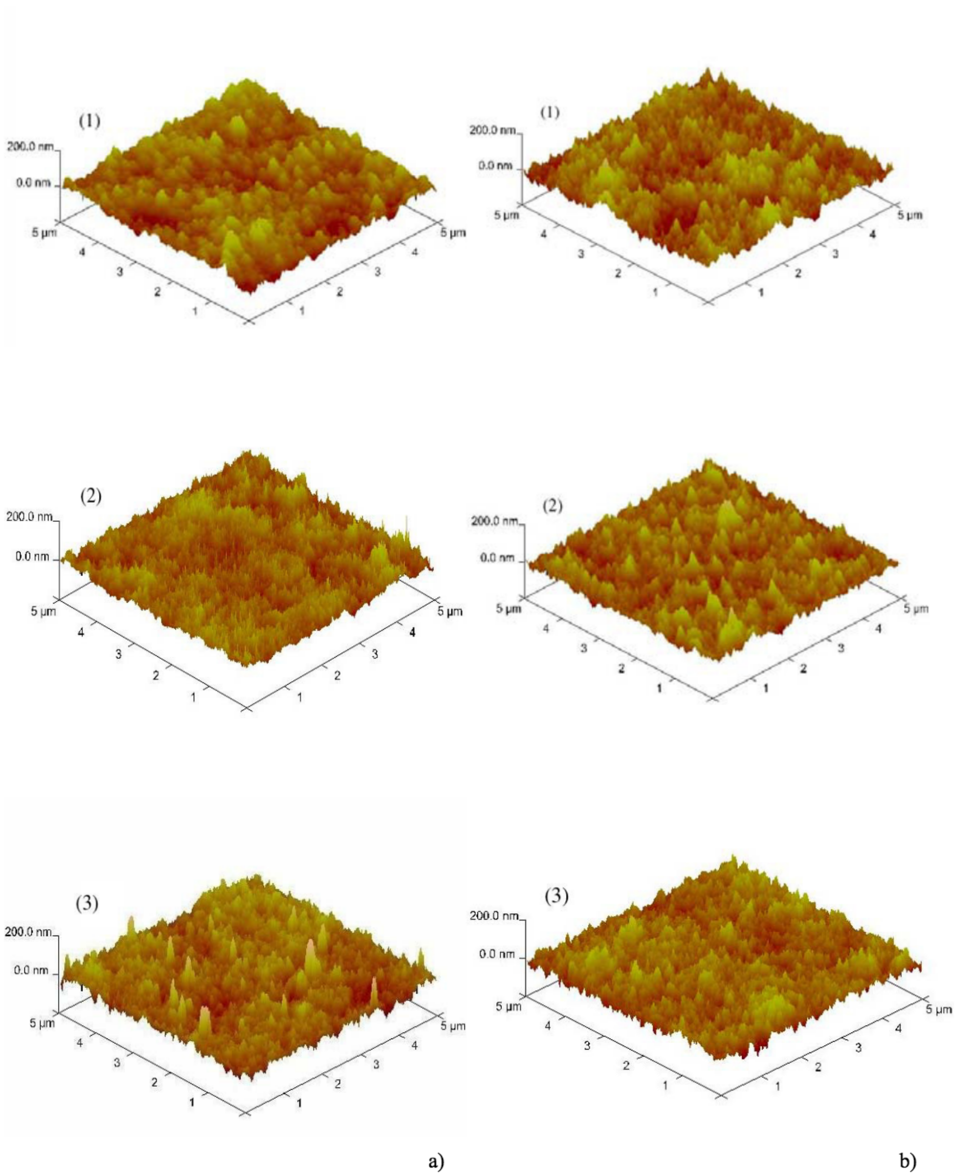


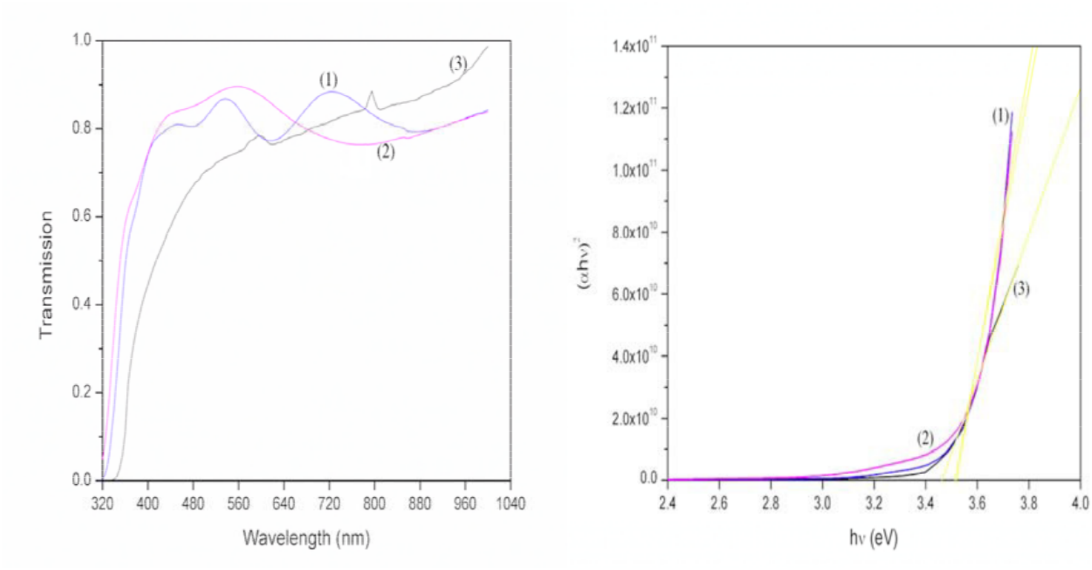
Fig. 3. AFM images of TiO_2 films deposited on a) glass substrate b) ITO coated glass substrate, using coating speeds of (1) 2000, (2) 5000 and (3) (2000-5000) rpm

Table 1. The roughness values of the coated films and substrates

Sample	Glass substrate	ITO coated glass substrate	TiO_2 coated on glass 2000 rpm	TiO_2 coated on glass 5000 rpm	TiO_2 coated on glass (2000-5000) rpm	TiO_2 coated on ITO 2000 rpm	TiO_2 coated on ITO 5000 rpm	TiO_2 coated on ITO (2000-5000) rpm
Roughness value	1.61 nm	2.86 nm	18.9 nm	17.1 nm	18.7 nm	20.8 nm	18.9 nm	18.7 nm

3.4. UV-VIS Spectroscopy

To obtain the optical band gaps of the thin films deposited with different spin rates on ITO coated glass substrate, transmittance spectra in the wavelength region of 320-1050 nm have been used which is shown in Figure 4. It is observed from high transmittance values of the films around 85% in the visible region, that these films have good homogeneity. Meanwhile, it can be deduced that for n-type TiO_2 films, the appropriate crystalline film is deposited on ITO coated glass substrate for 5000 rpm because of high transmittance value.



a) b)

Fig. 4. a) Transmission spectra b) Tauc plot of TiO_2 films deposited on ITO coated on glass substrates using coating speeds of (1) 2000, (2) 5000 and (3) (2000-5000) rpm

The absorption coeffcient α can be calculated by using the expression:

$$\alpha = - (1/d) \ln(I/I_0) \quad (1)$$

in which d is the thickness, I *and* I_0 is the intensity of transmitted and incident light perpendicular to the surface of the sample respectively [16].

The absorption coefficient α for a direct band gap related to the frequency of light is indicated by the following formula;

$$(\alpha h\nu) = A(h\nu - E_g)^{(1/2)} \quad (2)$$

where E_g is the optical band gap, $h\nu$ is the photon energy, A is a constant independent of photon energy [17-18]. Plotting the $(\alpha h\nu)^2$ versus $h\nu$, E_g can be obtained by extrapolation of the straight line on the energy axis.

The optical band gap of the films, obtained with single run spin coating on both substrates, exhibited direct bang gap energy of about $E_g \cong 3.5$ eV. The band gap value of the films obtained using two successive runs is calculated about 3.47 eV.

4. Conclusion

High porosity and nanoparticulate TiO_2 films with different thickness values were prepared by spin coating technique onto glass and ITO/Glass substrates for different spinning rates. Depending on the spinning rate and substrate nature, structural, morphological and optical characteristics of the films were compared. TiO_2 films deposited on ITO coated glass substrates all have crystalline nature, the better crystallinity is observed for 2000-5000 films. Also while the entire single run spin coated films on glass substrate show amorphous nature, the 2000-5000 films show crystalline behavior. These are attributed to both nature of substrate and thickness of the films. Structural and morphological characterizations of films show crack free anatase films with different thicknesses.

Through the optical characterization of the TiO_2 films, it was observed that the appropriate use of spin-coated TiO_2 nanoporous thin films of better crystallinity is 5000 rpm coating as n-type windows. From AFM images of spin-coated TiO_2 films, it is observed that while the deposited films are rougher for ITO substrates compared to glass substrates for 2000 and 5000 rpm spinning rates, for 2000-5000 rpm spinning rate there is no difference between roughness values of both substrates.

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