Study of influence of various rotation rates in deposition process on optical properties of SnO_2 thin films by spectroscopic ellipsometry technique

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Abstract

SnO_2 thin films deposited on glass substrates using sol-gel spin coating technique. Different rotation rates including 1800, 2100 and 2400 rpm were used to deposition. Deposited SnO_2 thin films were dried at 150^0 C for 10 min on a hot plate and then were annealed at 450^0 C for 1 h in an air furnace. Optical properties of the prepared SnO_2 thin films such as transparency, reflectance, refractive index and absorption coefficient were determined by using spectroscopic ellipsometry technique. The optical band gap energy of prepared SnO_2 thin films were measured. The SnO_2 thin films prepared with 2100 and 2400 rpm showed the highest (3.9ev) and the lowest (3.3ev) optical band gap values, respectively.

Keywords: SnO_2 thin film, sol-gel, spin coating, spectroscopic ellipsometry.

Introduction

Nowadays, technology of thin film deposition is so widespread. In general, a thin film is referred to a material or materials deposited on a surface which creates new structural, physical, optical, mechanical, etc. properties that may enhance the surface properties of the substrate for desired applications. The main features of a thin film are its sub-micronic thickness and super-large surface area versus the thickness. Thin films are mainly applied in the electronics, microelectronics and optoelectronics industries. During the last four decades, transparent conducting oxide (TCO) thin films have been received considerable attention and used for many applications in the modern technology due to their excellent characteristics such as high electrical conductivity and high optical transparency. SnO_2, ZnO, CdO, In_2O_3 and TiO_2 are among the most important TCO thin films (Stadler, 2012). TCOs are widely used in gas sensors (Das and Jayaraman, 2014), solar cells (Kwak et al, 2011. Ian and Bu 2014), photovoltaic or optoelectronic devices (Beyer et al, 2007), as reflective coatings and in smart windows (Durrani et al, 2004), plasma and touch screen displays (Betz et al, 2006) and lithium batteries (Zhao et al, 2006).Tin oxide (SnO_2), as a considerable TCO, showing a tetragonal rutile structure is intrinsically an n-type semiconductor with a wide direct band gap 3.6-4 ev. in the visible light. It is also non-toxic, economic, electrochemically stable that has good productivity, high electrical conductivity, high transparency in the uv-visible region and high reflectance in infrared region (Benouis et al, 2014). These unique properties of SnO_2 thin films make them an ideal candidate for use in optoelectronic devices (Kose et al, 2011 and Khuspe et al, 2013). So far many studies have been conducted for the characterization of optical and electrical properties of SnO_2 thin films (Wu et al, 2010 and Gul et al, 2015). SnO_2 thin films can be prepared using different techniques such as spray pyrolysis (Serin et al, 2006), magnetron sputtering (Bansal et al, 2014), sol-gel (Ozugur Uysal and Arier, 2015). Results show that properties of thin films are extremely sensitive to the preparation conditions and deposition method. Among these deposition techniques, the sol-gel method has attracted particular attention due to its advantages such as simplicity, low cost, easy availability, facultative processing temperature, ability to produce porous structures and high production efficiency (Talebian et al, 2013 and Ma et al, 2013). There are several methods for analyzing and characterization of thin films, for instance, X-ray fluorescence spectroscopy (XRF), X-ray diffraction spectroscopy (XRD), scanning electron microscope (SEM), atomic force microscope (AFM) and spectroscopic ellipsometry (SE). In the past two decades, SE has been shown to be a powerful and non-destructive technique for the characterization of thin films. This technique is sensitive to many parameters of the thin film such as thickness, surface roughness, interface properties and the substrate. SE is capable to measure the thickness and the complex dielectric function of a multilayer system, simultaneously. Therefore it is a robust technique to evaluate the band structure of nano-scale semiconductors through determining their complex dielectric function. SE is widely used to determine optical constants of thin films in the wavelength range of ultra-violet, visible and infrared light (Atay et al, 2010). In this research, SnO_2 thin films deposited on glass substrates were prepared by sol-gel spin coating method with different rotation rates and their optical properties were investigated by using SE technique.

Experimental

SnO_2 thin films deposited on glass substrate using sol-gel spin coating technique. Different rotation rates of 1800, 2100 and 2400 rpm were used for deposition. 0.35 molar SnO_2 solution prepared by dissolving 0.789 g tin (II) chloride dehydrate [$SnCl_2.2H_2O$, M_W = 225.63, Merck] in 10 ml pure ethanol. Then, the solution stirred at 80^0 C for 3 h and 1 h to reach RT to yield a homogeneous and clear solution. The obtained solution was aged for 36 h at RT before spin coating. It should be noted that glass substrates were pre-cleaned by acetone and deionized water and completely dried using an air gun before spin coating deposition. Deposition on glass substrates were conducted using spin coating with rotation rates of 1800, 2100 and 2400 rpm, followed by drying at 150^0 C for 10 min on a hot plate. Finally, all samples were annealed at 450^0 C for 1 h in an air furnace. The proposed reactions between the involved chemical materials during the fabrication of SnO_2 thin films are as follows:

$$\begin{array}{l} SnCl_2\,.2H_2O + CH_3CH_2OH \rightarrow Sn(OH)_2 + CH_3CH_2Cl \\ Sn(OH)_2 \xrightarrow{\text{Pre-heating/150 C}} SnO\ (\text{metastable}) + H_2O \\ SnO\ (\text{metastable}) \xrightarrow{\text{Annealing/ 450 C}} SnO_2\ (\text{stable}). \end{array} \tag{1}$$

An spectroscopic ellipsometery machine of SE800DUV model was used to investigate the optical properties of prepared SnO_2 thin films, in the wavelength range of 300-800 nm. Ellipsometry parameters, (ψ,Δ) were recorded for all SnO_2 thin films in the fixed angle of incidence of light, 70^0. The measurements were conducted at room temperature.

Results and discussions

In this work, optical properties of prepared SnO_2 thin films with various rotation rates of 1800, 2100 and 2400 rpm were studied using SE technique. Ellipsometry is an optical measurement technique that characterizes light reflection from thin film samples. The key feature of ellipsometry is that it measures the change in polarized light upon light reflection on a sample. The name 'ellipsometry' comes from the fact that polarized light often becomes 'elliptical' upon light reflection. Ellipsometry measures two values (ψ,Δ) by changing the wavelength of light, where represent the amplitude ratio ψ and phase difference Δ between p- and s-polarized light waves. The (ψ,Δ) measured from ellipsometry are defined from the ratio of the amplitude reflection coefficients for p- and s-polarizations (Atay et al, 2010):

$$\rho \equiv r_p / r_s \equiv \tan\psi \exp(i\Delta) \tag{2}$$

Where r_p and r_s are the amplitude reflection coefficient for light polarized in the p- and s-plane of incidence, respectively. In ellipsometry, the angle of incidence is chosen so that the sensitivity for the measurement is maximized. It should be mentioned, at normal incidence, the ellipsometry becomes impossible, because p- and s-polarized lights become indistinguishable (Fujiwara 2007). In this work measurement was conducted in the wavelength range of 300-800 nm in the fixed angle of incidence of 70^0. Ellipsometry cannot determine optical constants or the thickness of a thin film directly. The obtained (ψ,Δ) can be related to the thin film characteristics through mathematical functions. Therefore, an analysis based on a model must be done to obtain these parameters from the (ψ,Δ) measured by ellipsometry. It is the step named definition of the optical model. The optical model for SnO_2 thin films is defined as air / surface roughness layer / SnO_2 thin film / glass substrate structure. Data analysis was conducted using linear regression analysis. Effective medium approximation was used for the surface roughness layer fitting. The experimental (ψ,Δ) spectra measured by ellipsometry have been fitted to the optical model defined above (fitting error (MSE) «1). Figure 1 shows the experimental and fitted data of (ψ,Δ) for SnO_2 thin films with different rotation rates.

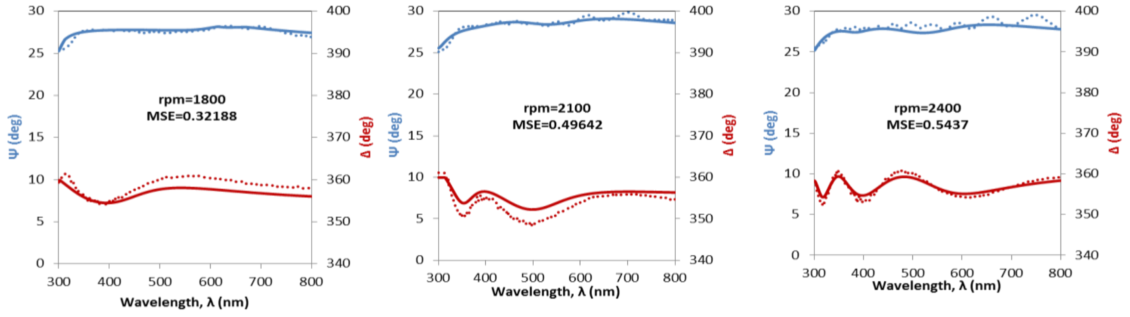

Figure 1. The experimental (dotted lines) and fitted (solid lines) (ψ,Δ) spectra for SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm.

The optical transmittance (T) and reflectance (R) percentages of prepared SnO_2 thin films with rotation rates of 1800, 2100 and 2400 rpm are shown in figure 2, respectively. It can be seen that the SnO_2 thin film prepared with 1800 rpm has higher transmittance and lower reflectance compared with the two other thin films prepared with 2100 and 2400 rpm, may be due to the higher crystallite size, formation of smoother surface structure and minimum scattering loss. Additionally, The SnO_2 thin film prepared with 2100 rpm has lower transmittance and higher reflectance. Therefore, it can be deduced in small range of rotation rates there is no regular pattern for variation of optical transmittance and reflectance. Also, it can be observed for all SnO_2 thin films transmittance increase and reflectance decrease, with increase of the wavelength from 300 to 800 nm, regardless to the rotation rate value.

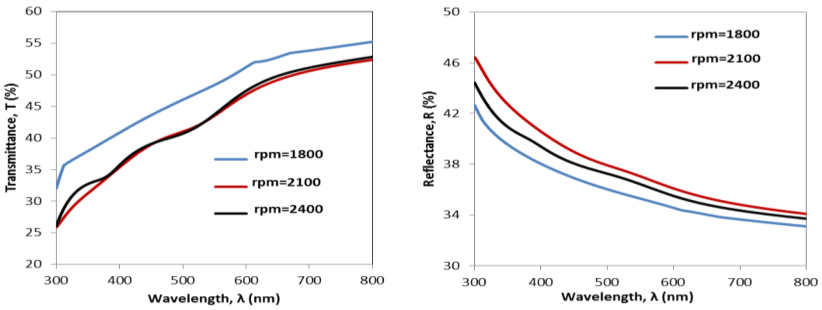

Figure 2. The optical transmittance (T) and reflectance (R) percentages of SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm versus wavelength of light.

Figure 3 shows the dependence of refractive index (n) values of the SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm on the wavelength in the region of 300-800 nm. The folds visible on the figure can be due to the multiple interference of the light from the interfaces of ambient/SnO_2 thin film and SnO_2 thin film/glass substrate. The range of n values for prepared SnO_2 Thin films are between 4.54 and 11.26. It can be observed that SnO_2 thin films prepared with 2100 and 2400 rpm have the lowest and the highest refractive index values, respectively. The n value for all thin film samples decreases with increase of wavelength of light from 300 to 800 nm.

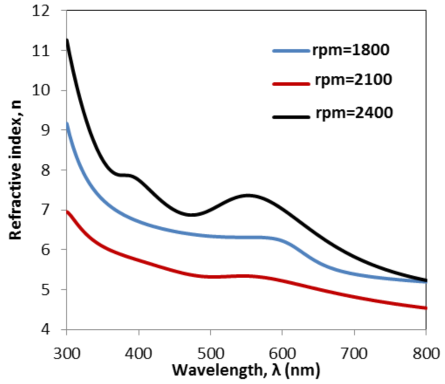

Figure 3. The refractive index (n) of SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm versus wavelength of incidence light.

The absorption coefficient (α) of SnO_2 thin films can be calculated from $4\pi k/\lambda$ formula, where k is the extinction coefficient of the thin film measured by ellipsometry and λ is the wavelength of incident light (Fujiwara 2007). In figure 4 the absorption coefficient (α) of SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm versus wavelength are shown. It can be seen the film prepared with rotation rate of 2400 rpm has the highest α values. The SnO_2 thin film prepared with

2100 rpm has the lowest α values maybe due to the formation of more voids on this layer. The results obtained for n and α values are consistent with the results for R and T values.

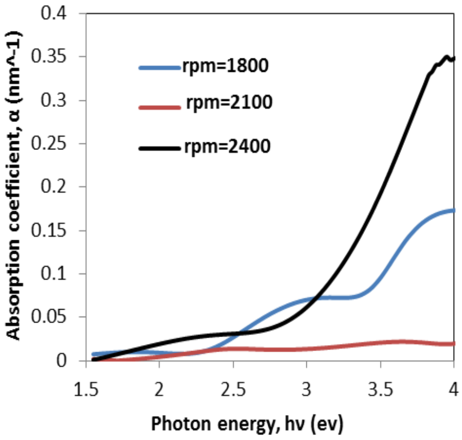

Figure 4. the absorption coefficient (α) of SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm versus wavelength of light.

The influence of rotation rate on the optical band gap (E_g) of SnO_2 thin films can be evaluated using the well-known equation (Atay et al, 2010):

$$\alpha h\nu = C_1(h\nu - E_g)^m \tag{3}$$

where α is the absorption coefficient, hν is photon energy, C_1 is a constant and m=1/2 for the direct allowed transitions. Figures 5 shows the plot of $(\alpha h\nu)^2$ versus hν. E_g are determined based on the linearization of equation (3) by extrapolating the straight line portion of these plots to the energy axis. The range of photon energy is between 1.5 and 4.2 ev. From figure 5, it is obvious that E_g values for the SnO_2 thin films prepared with 1800, 2100 and 2400 rpm are 3.4, 3.9 and 3.3 ev, respectively. Since n is strongly connected with band gap energy, it can be also conclude that the material with smaller E_g has a larger value of n. the results here confirmed that. The SnO_2 thin films with 2400 and 2100 rpm have the smallest and largest band gap energy value, respectively.

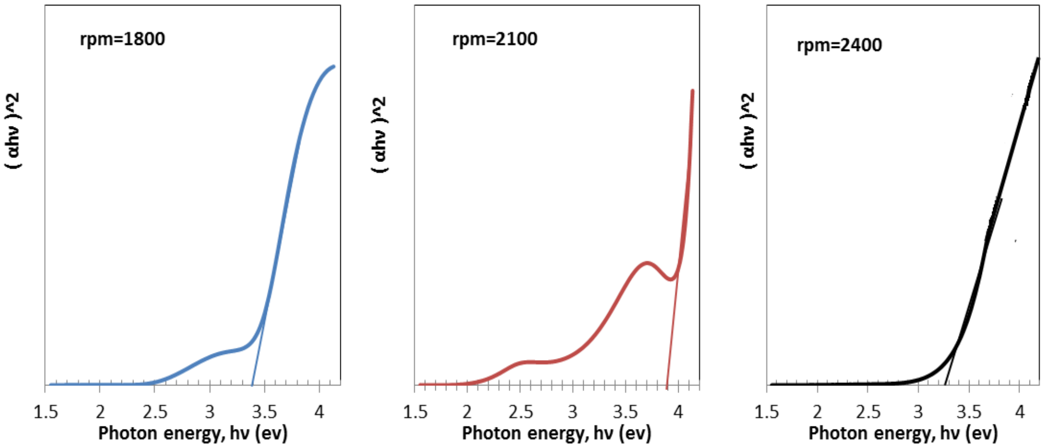

Figure 5. The allowed direct optical band gap (E_g) for SnO_2 thin films prepared with rotation rates of 1800, 2100 and 2400 rpm.

Conclusions

Sol- gel spin coating method was used to deposition of SnO_2 thin films on glass substrates. Different rotation rates of 1800, 2100 and 2400 were used for deposition. Optical properties of the prepared SnO_2 thin films including transparency, reflectance, refractive index and absorption coefficient were determined by using spectroscopic ellipsometry (SE) technique. The results revealed that in the low range of rotation rates (1800-2400) of spin coating deposition process, there is no regular pattern for variations in the optical constants, so that the SnO_2 thin film prepared with 2400 rpm showed the highest refractive index and absorption coefficient values, while the one prepared with 2100 rpm showed the lowest values. The SnO_2 thin film prepared with 1800 rpm had the highest transparency percentage of 55% and the lowest reflectance value of 33%. The optical band gap energy of the SnO_2 thin film prepared with 2100 rpm had the highest E_g of 3.9 ev. The results confirmed that SnO_2 thin films with the smaller band gap energy have the larger refractive index. It may be expected that in a higher range of rotation rates, there is more regular pattern for variations of optical constant of SnO_2 thin films deposited on glass substrates using sol-gel spin coating method. Therefore, changing the rotation rate of spin coating deposition may be used to modulate band gap energy and hence the material may be used in optoelectronic devices.

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