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Electrochemical, Structural, and Optical Properties of SnO_2 thin films

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ABSTRACT

SnO_2 thin films were electrodeposited on fluorine tin oxide substrate in nitric acid solution. The potential was swept from -0.4 to -1.6V with a rate of 50 mV/s. The films were found uniform, adherent to the substrate and amorphous. The XRD patterns reveal that after heat treatment at 600°C for 1h, the films turn out to be crystalline in nature. Indeed, the film becomes composed of SnO_2 nanocrystallite with a casseterite tetragonal structure. The nanocrystallite size is about 50 nm. The films thickness was found to be approximately 592nm and 563 nm for as-deposited and heat-treated (600°C) SnO_2 thin films, respectively. Some optical parameters of these films such as refractive index (n), extinction coefficient (k), absorption coefficient (α) and band gap were studied. Theses parameters were deduced by Swanepoel method in the wavelength range 300-800 nm using optical transmission data. It is shown that the band gap was found to increase from 4 eV to 4.036 eV after heat treatment at 600°C.

Electrochemical results obtained in aqueous medium: KOH, KI, $LiClO_4$ and H_2SO_4, shows a good electrochemical stability of these oxides and the curves of electrochemical analysis make it possible to have an outline on the kinetics of the formation of these layers.

Index Terms— Thin films; Optical properties; band gap; electrodeposition , cyclic voltammetry, KOH, KI, $LiClO_4$

1. INTRODUCTION

Tin oxide is one of the most widely studied oxide semiconductor owing to their exceptional properties. Indeed, in the last decade it has attracted an enormous attention due to two main reasons namely: the high transparency in the visible region and high conductivity. These two characteristics make SnO_2 very suitable as transparent conductive electrodes. Besides, tin oxide has excellent physical and chemical properties when the particle size or grain size is reduced to nanometer scale. With high transmittance in visible light and good electric characteristics, tin oxide is widely applied as an important material for many fields. The nanocrystalline SnO_2 is considered as a key material for photovoltaic device [1], transparent conductive electrode [2], gas sensor [3,4], and anode materials of secondary lithium battery [5]. The methods that are used more often for depositing SnO_2 are sputtering [5], evaporation [6], electrodeposition [7], chemical vapour deposition [8,9], sol–gel process [10–11] and pyrolysis of stannic compounds [12]. Among these methods, electrodeposition offers a number of combined advantages for deposition of thin films such as the simplicity and low cost equipment, precise control of film thickness, composition and deposition rate, low temperature process nature and the possibility of film formation on substrates of complicated shape. The co-deposition nanocrystalline of SnO_2, Sn and SnO occurs for anodic or cathodic electrodeposition. As example, it is shown that the electrodeposition in nitrate solution [6,7] leads to small amount of metallic Sn co-deposited with nanocrystalline SnO_2. In this work we have shown that, it is possible to obtain a nanocrystalline SnO_2 thin film with suitable structural and optical properties by cyclic voltammetry in tin chloride solution and the film so prepared was found to be free of components like Sn and SnO.

2. EXPERIMENTAL

2.1 Preparation and characterization of the SnO_2 film

Cyclic voltammetry experiment was performed using a voltalab PGZ301 and a voltamaster 4 logiciel. The

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deposition cell was a three-electrode electrochemical cell, in which a Pt foil was used as counter-electrode, Ag/AgCl as reference electrode and SnO_2:F as a conducting glass with a sheet resistance of 7,9 Ω/□ and 78.50% transmittance in the visible region. The deposition solution is composed of 25mM $SnCl_2$ -$2H_2O$ (Riedel-de Haën, 99.8%), 75mM nitric acid (J.T. Backer, A.C.S. reagent) balanced by redistilled water. The pH of the solution was 1.50. The deposition is carried out by potential cycling from -0.4 to -1.6V with a rate of 50 mV/s. The number of cycling was 20 times. The SnO_2:F substrates were ultrasonically cleaned in acetone, 2-propanol and water each for 15 min. Then, SnO_2 films were deposited on these substrates. Finally, these films were subjected to heat treatment at 600°C in air for 1h to obtain crystalline SnO_2 thin films. The film structure was investigated by X-ray diffraction (Siemens D8 Advance) with Cu Kα radiation. The optical transmittance of the SnO_2 films was measured in the wavelength range 300–800 nm by spectrophotometer (UV–VIS– UNICAM 300) using a logiciel VISION 32.

2.2. Structural properties

The XRD of the as synthesized and heat-treated (600°C for 1h) SnO_2 thin films prepared by electrodeposition technique are shown in Fig.1(a) and 1(b) respectively. It shows that before heat treatment, no significant peak appears meaning that the film structure is amorphous. After heat treatment, peaks with high intensity appear. Theses peaks correspond to the planes (200), (110), (211) and (310) indicating that the structure is casseterite tetragonal. As the peak of (200) plane is more intense, the film preferential orientation is <200>. Similar results were reported for sol–gel deposited tin oxide films from $SnCl_2$ precursor [13]. The lattice constants, a and c can be estimated from XRD pattern using the Scherrer's formula [14]:

$$D=0.9\lambda/B\cos\theta \qquad (1)$$

Where θ is the Bragg's diffraction angle; B is the broadening of diffraction line at half its maximum intensity and λ is the wavelength of X-rays. The lattice parameter values a and c as well as the crystallite size D for these samples are presented in Table 1. The calculated lattice constants (a and c) are found match well with the standard JCPDS data card [17]. This indicates that the film grains are not strained which may be due to low concentration of the native imperfections such as oxygen vacancies and vacancy clusters.

Table 1. Structural parameters of electrodeposited tin oxide thin films: (A) as-deposited and (B) after heating at 600°C for 1 h in air.

	Lattice parameters		(hkl) values	Grain size from XRD (nm)
	a (Å)	c (Å)		
Film A			Amorphous	
Film B	4.7396	3.1933	110 200 211	9.479

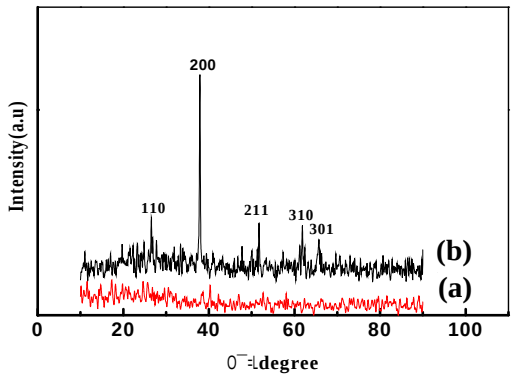

Fig.1. XRD patterns of electrodeposited SnO_2 thin films: (a) as deposited and (b) after heating at 600°C for 1 h in air.

3. OPTICAL PROPERTIES

The plot of transmittance versus wavelength for as-synthesized and heat-treated (600°C for 1h) SnO_2 thin films is shown in Fig 2. The films have interference fringes in the 300–600 nm range indicating a good homogeneity and thickness uniformity of the films [15]. The interference fringes are the result of the interference of the light reflected between air-film and film-substrate interfaces [16]. As can be observed that the heat treatment accentuate the interference effects which become more prominent. This may be due to the improvement of quality of interfaces related to the crystallization of film. The film heat-treated at 600°C for 1 h has a transmittance value of 77% at wavelength of 800 nm, whereas a lower value (68%) was measured for as-deposited film. This improvement of optical transmittance with the heat-treatment can be due to the crystallization of the films as evidenced by XRD pattern analysis. The crystallization probably reduces the light scattering resulting in better transparency of films [17].

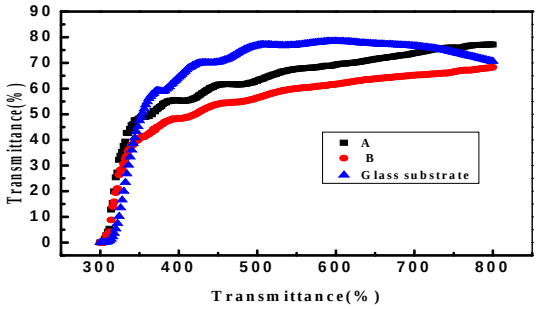

Figure (2): Transmittance of films (A) as-deposited (B) heated at 600°C for 1 h in air.

3.1 Determination of optical constants

It is well known that the optical constant such as refractive index (n) can be deduced from the transmittance spectrum fringe patterns using Swanepoel method [18, 19]. According to this method, refractive index and extinction coefficient can be plotted as a function of wavelength and are shown in the figure 3. From the spectra it is observed that the refractive index notably increase after heat treatment. On the other hand, the extinction coefficient decreases in the visible region indicating weaker photon absorption by electrons transitions to levels within the band gap where less inter band gap defect levels could be present. The same behaviour was reported when the tin oxide is deposited onto hot substrates [20]. The high value of refractive index found makes these films suitable for a great number of applications, such as Dye-sensitized solar cell, antireflection coatings, etc. These values are similar to those which correspond to a casseterite tetragonal structured film. The equations used for the calculations of optical constants are obtained from reference [18]. The film thickness is calculated from the figure 3a using the following equation
[18]:

$$d=\lambda_1\lambda_2/2[\lambda_1 n_2-\lambda_2 n_1] \quad (2)$$

The film thickness d was found to be about 592, 563 nm, for as-deposited films and after heat treatment, respectively. This decrease of film thickness after heat treatment can be attributed to the evaporation of H_2O in accordance with the literature [21].

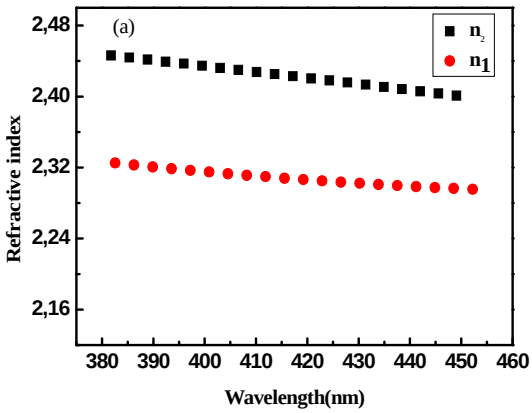

Figure (3.a): Variation of refractive index (n) with wavelength (λ) in tin oxide thin films (n_1) before, (n_2) after the heat treatment

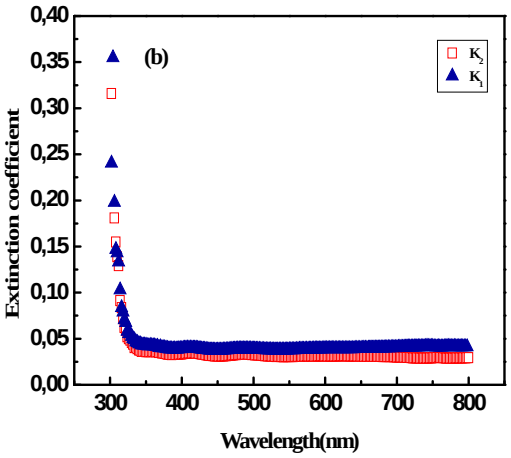

Figure (3.b): Variation of extinction coefficient (k) with wavelength (λ) in tin oxide thin films(K_1) before, (K_2) after the heat treatment.

3.2. Optical band gap calculation

The optical band gap values of the thin film SnO_2 was calculated by tauc's extrapolation method [18], and compared to the plot of $(\alpha h\nu)^2$ vs hν for the determination of direct band gap Eg (Fig.4). The band gap is extracted from the following relation [18]:

$$(\alpha h\nu)^2=A(h\nu-Eg) \quad (3)$$

Where α is the absorption coefficient, A and Eg are constant and band gap of the material, respectively. The figure 4 shows that a higher optical band gap could be obtained by increasing the annealing temperature. The direct optical band gap (Eg) values calculated in the present work were 4.0 and 4.036 for SnO_2 thin films, as deposited and annealed at 600°C respectively. Similar behaviour is

observed for ITO films grown on glass at room temperature prepared by electron beam evaporation [22]. The increase of band gap after heat treatment can be related to the increase of the mobility and carrier density when the amorphous film becomes partially crystalline [22]. The band gap values found in this work are close to those reported in the literature [23]. It is well known that the band gap is about 2.7 eV and 3.9 eV for SnO and SnO_2, respectively [22]. As the values of this parameter found in this work are very close of that SnO_2, we can conclude that the as-deposited and heated films are composed mainly by SnO_2.

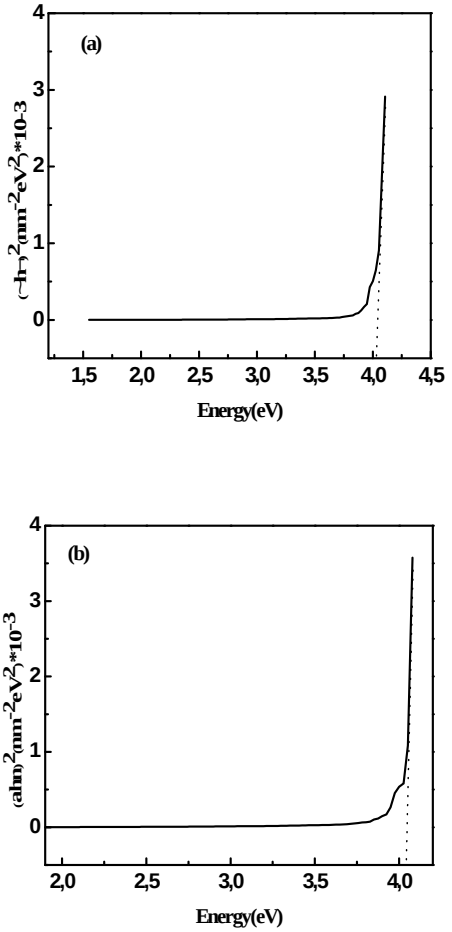

Figure 4. The plot of (αhν)2 versus hν to determine the band gap of SnO2 thin films (a) before, (b) after the heat treatment.

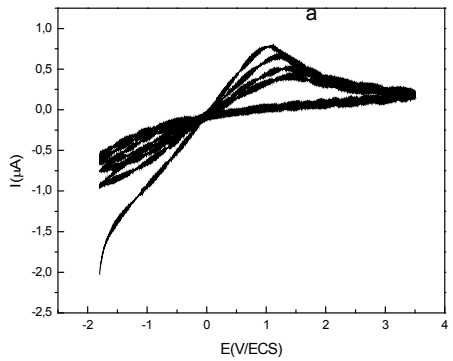

***Figure* 5** Cyclic voltammogram of thin film of SnO_2 in a H_2SO_4 solution at : 0.1M and V = 100 mV /s

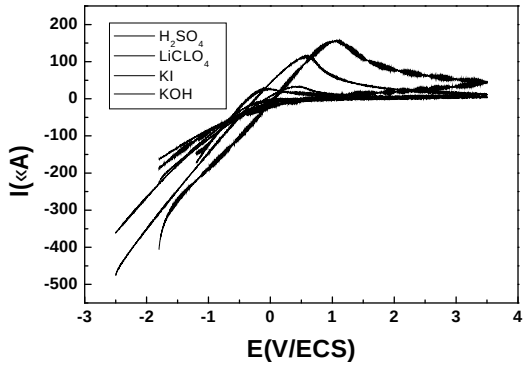

Figure 6 : Cyclic voltammogram at 100 mV / S: H_2SO_4, $LiClO_4$, KI and KOH pH: 1.17, 7.3394, 7.94, and 4.38 respectively

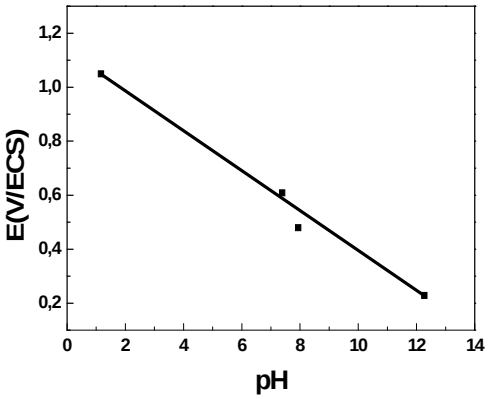

Figure 7: Variation of the potential of the anodic peak of SnO_2 with the pH solution..

Electrochemical results obtained in aqueous medium: shows a good electrochemical stability of thin films SnO_2

CONCLUSION

A SnO_2 amorphous film was deposited on glass by voltammetry cyclic in tin chloride solution. The structural and optical characteristics of the deposited SnO_2 thin films were analyzed before and after heat treatment at 600°C. It is observed that the heating improves the optical transmittance due to the crystallization of the films. It is evidenced by XRD patterns that the heated film exhibits a casseterite crystalline structure. In addition, it is shown that it is composed only by the phase of SnO_2. It is noticed that the refractive index as well as the band gap are increased after heating at 600°C. This is attributed to the crystallisation of the film. Finally, it is more reasonable to conclude that the change in film composition and structure could more affect the optical parameters. Electrochemical results obtained in aqueous medium: KOH, KI, $LiClO_4$ and H_2SO_4, shows a good electrochemical stability of these oxides and the curves of electrochemical analysis make it possible to have an outline on the kinetics of the formation of these layers.

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