International Journal of Materials and Chemistry 2012, 2(4): 173-177
DOI: 10.5923/j.ijmc.20120204.10

Properties of Amorphous SnO_2 Thin Films, Prepared by Thermal Evaporation

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Abstract Tin oxide (SnO_2) thin films of thickness in the range 100-600 nm are prepared on glass substrates by thermal evaporation at ambient temperatures. The films are characterized by recording their transmittance measurements, X-ray diffraction (XRD) patterns, scanning electron microscope (SEM) images and energy dispersion X-ray analysis (EDAX). It is found that the films have high transmittance and non-sharp absorption edge. XRD diffractograms showed that the films are amorphous and the SEM micrographs depicted that the surfaces are smooth, uniform and well covered with the material. The EDAX analysis showed that the films are deficient in oxygen. Indirect optical bandgap energy is determined and Urbach tailing in the bandgap is observed and the width of the tail which is related with disorder and localized states is estimated.

Keywords Transparent Conducting Oxides (TCOS), Amorphous Tin Oxide Thin Films, Optical Properties, Urbach Tail, Gas Sensors

1. Introduction

$SnO_2$is an n-type wide bandgap semiconducting material with direct bandgap energy of 4 eV and indirect bandgap of 2.6 eV[1], where inherent oxygen vacancies act as an n-type dopant[2]. Tin oxide thin films have been used for transparent electrodes in photoelectric conversion devices namely amorphous silicon solar cells, liquid crystal display, gas discharge display, etc.[3]. Perfectly amorphous thin SnO_2 films show good electrical response to reducing gases in air and could hence be applied to construct semiconductor gas sensors where the metal oxide films function as a monograin-eqivalent active layer[4]. Amorphous SnO_2 can also be used in extended gate field-effect transistors (EGFET) as pH sensor, where the sensitive part is made of SnO_2/Al structure. This device can be used to detect and to quantify any kind of substances that can produce or consume protons like an enzymatic reaction, therefore showing a large range of applications as biosensors[5].

There are different methods to prepare SnO_2 films such as, atomic layer deposition (ALD)[6], reactive magnetron sputtering[7], chemical vapor deposition ([8],[9]), dip coating[10], spray pyrolysis (SP) ([3],[11-14]), and evaporation[8]. Thermal evaporation method was choose to produce SnO_2 thin films in this work because the deposition by this technique does not present any compositional problems, beside the fact that it is a low temperature producing amorphous films. To increase this probability the technique, which increases the probability of films were deposited at ambient temperature.

In this work the properties of amorphous SnO_2 thin films are investigated by studying their structure, morphology, composition and transmittance at room temperature. The films were characterized by X-ray diffraction (XRD), scanning electron microscope observations, energy dispersive analysis by X-ray (EDAX), and transmittance measurements. The indirect bandgap of the films and Urbach tailing were estimated and discussed.

2. Experimental Part

Undoped SnO_2 thin films are deposited by thermal evaporation at ambient temperature on glass substrates of dimensions ($6\times2.6\times0.1 cm^3$) in a high vacuum system ($\sim10^{-5}$ mbar) provided with a Turboe pump. The substrates are cleaned in methanol, followed by distilled water. The evaporation rate is about 10 Å/s and it is measured by a cooled quartz crystal monitor. The distance between the source and the substrate is about 30 cm. Films of thickness 50-600 nm are produced through different individual evaporations. The films showed light brown colour that becomes darker with film thickness.

The transmittance of the films is measured by using a double beam Shimadzu UV 1601 (PC) spectrophotometer with respect to a piece of glass similar to the substrates in the wavelength range 300-1100 nm. The thickness of the films is estimated from the interference maxima and minima in the transmittance by using the method of Alvin[15]. X-ray

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Published online at http://journal.sapub.org/ijmc

measurements are made with a Philips PW1840 Compact X-ray diffractometer system with Cu K_α (λ = 1.5405 Å). The SEM images are taken by a FEI scanning electron microscope (Inspect F 50), which is supplied by energy dispersive analysis by X-rays (EDAX), so the compositional analysis of the films is performed by the same system.

3. Results and Discussion

Fig.1 displays the X-ray diffractograms for two SnO_2 thin films of different thickness 200 and 600 nm, deposited on glass substrates at ambient temperature. Both diffractograms showed a broad hump including the positions of the (1 1 0) and (1 0 1) lines, indicating that the films have amorphous structure. It is noticed that the peak of the hump for the thicker film is centred at about 2θ = 29°, while that of the thinner one is centred at about 2θ = 28°. Beside this the width of the hump of the thinner film is larger than that of the thicker one, and hence the full widths at half maximum FWHM are 4.5 and 5.0° for the thicker and thinner films respectively. From these results we conclude that the thicker film is closer to the transformation from the amorphous phase to the polycrystalline phase than the thinner one.

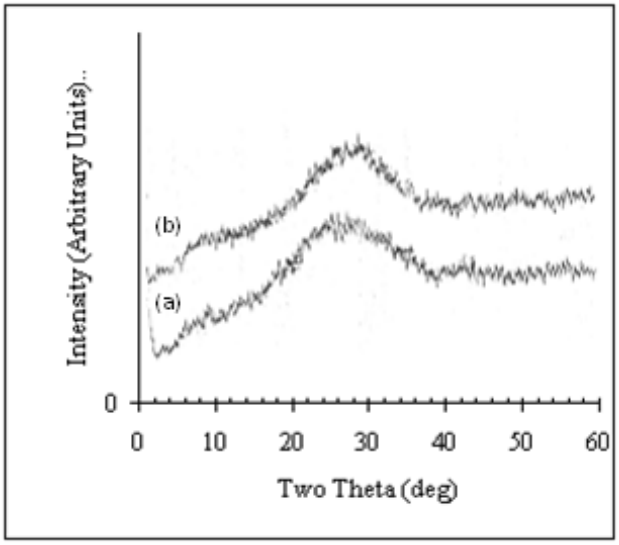
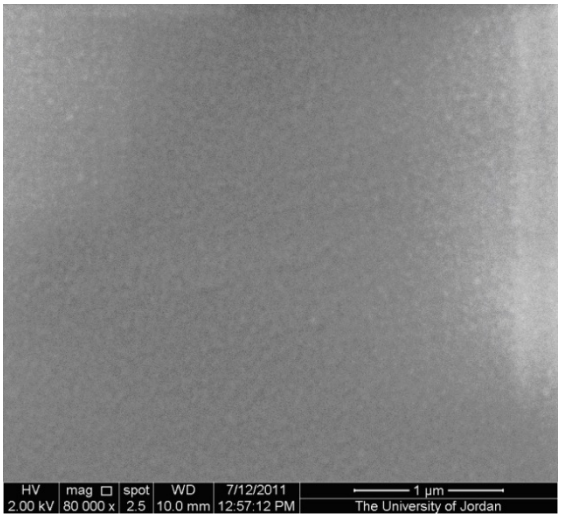
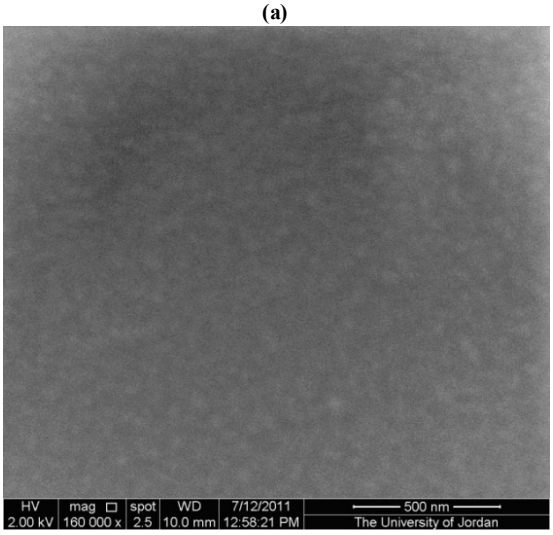


Figure 1. X-ray diffractograms of two thermally evaporated SnO_2 thin films with thickness a) 200 nm. b) 600 nm

Fig.2 shows the SEM micrographs at two magnification values (at 80000X and 160000X) of two films of different thickness 300 nm (Fig.2a and b) and 400 nm (Fig.2c and d). The SEM images show smooth, featureless surfaces in agreement with the amorphous structures, observed by XRD patterns. No evidence of granularity as would be seen for a crystalline film.



(a)



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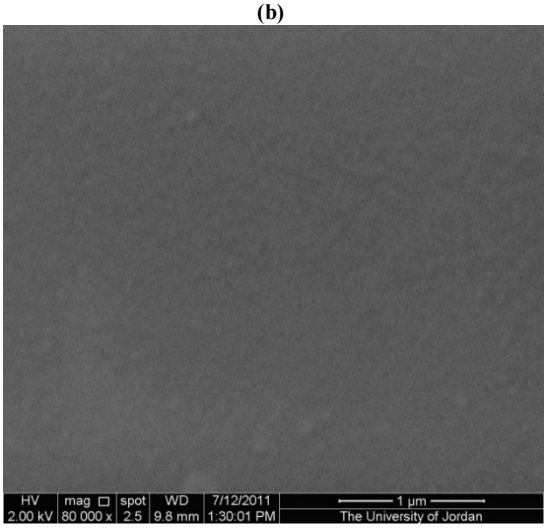

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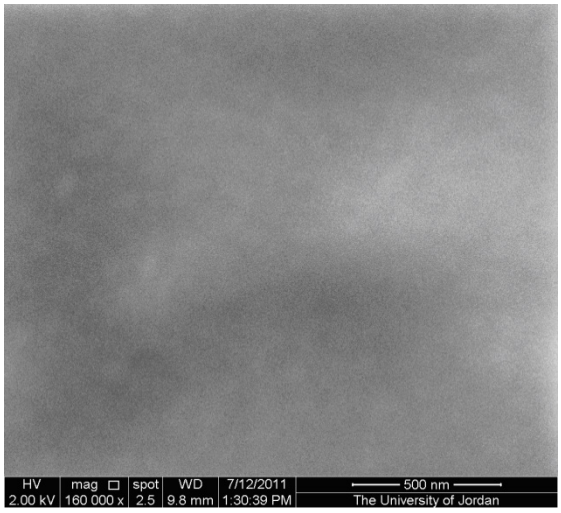

(d)

Figure 2. SEM micrographs at two magnifications of two thermally evaporated SnO_2 thin films of thickness 300 nm (a) and (b); and 400 nm (c) and (d)

Fig.3 depicts the EDAX spectra for the two films of thickness 300 and 400 nm with the SEM photos to show the positions where the compositional analysis was performed. The elemental concentrations of tin and oxygen are summarized in table 1.

Table 1. Results of the EDAX compositional analysis obtained for two thermally evaporated SnO_2 thin films with different thickness

t(nm)	Concentration of O wt.%	Concentration of Sn wt.%
300	62.96±22.2	37.04±14.1
400	55.81±18.5	44.19±15.1

As seen from the data presented in Table 1, the films are deficient in oxygen, where the ratio of oxygen to tin is 1.7 and 1.26 in the thinner and thicker films respectively, while the stoichiometric ratio is 2. This means that there are inherent oxygen vacancies and hence the films are n-type .

Fig.4 shows the transmittance of the films with different thickness measured at room temperature. The transmittance is high in the visible and infra-red regions and reaches about 100% there for most of the films in the set. Interference fringes which are indication on the uniformity of the films are used to estimate film thickness as mentioned before.

The observed broadening of the absorption edge towards longer wavelengths is due to the disorder effect, which is always seen in amorphous films.

It is known that, in the vicinity of the fundamental absorption edge, for allowed direct band-to-band transitions, neglecting exciton effects, the absorption coefficient is described by[16];

$$\alpha(h\nu) = \frac{K(h\nu - E_g^{opt})^m}{h\nu} \quad (1)$$

where α is the absorption coefficient, h is Planck's constant, ν is the frequency of the radiation, K is the characteristic parameter (independent of photon's energy) for respective transitions, $h\nu$ denotes photon's energy, E_g^{opt} is the optical energy gap and m is the number which characterizes the transition process, where $m = 2$ for most amorphous semiconductors (indirect transition) and $m = 1/2$ for most of crystalline semiconductors (direct transition).

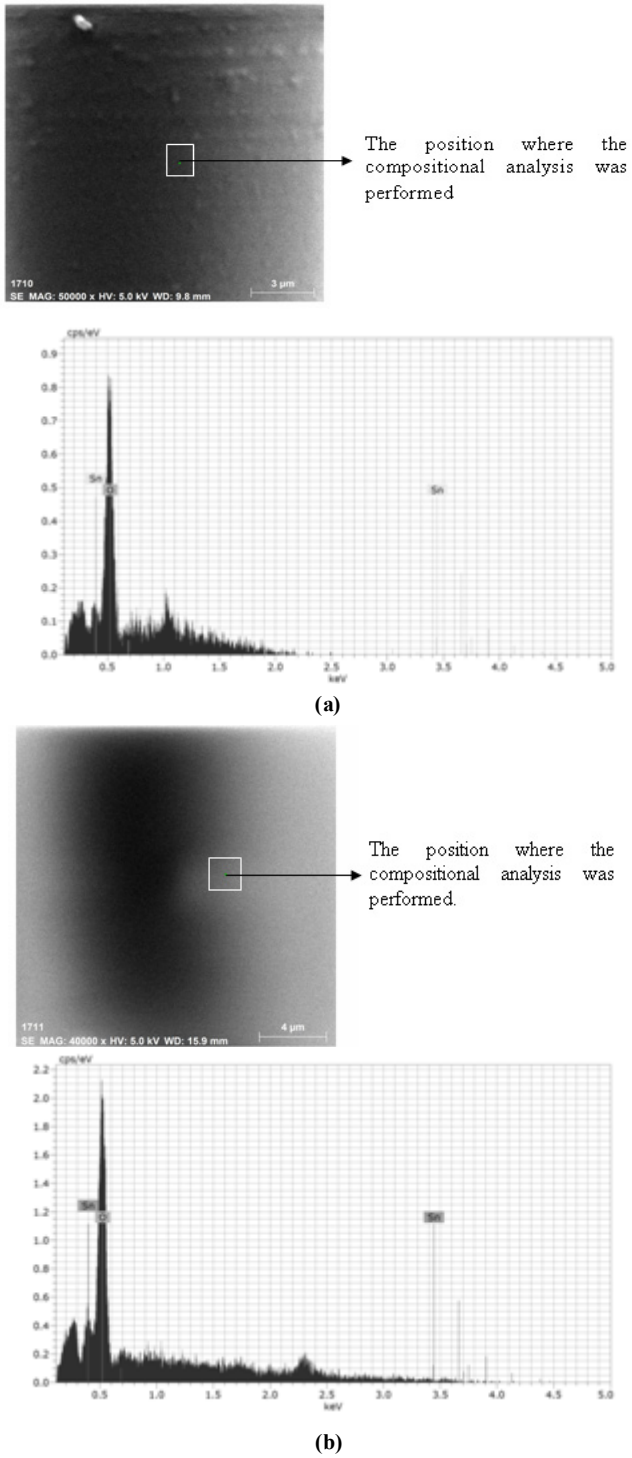

Figure 3. EDAX patterns for amorphous SnO_2 thin films and accompanied SEM images to show the point at which the compositional analysis is performed. a) Film thickness = 300 nm. b) Film thickness = 400 nm

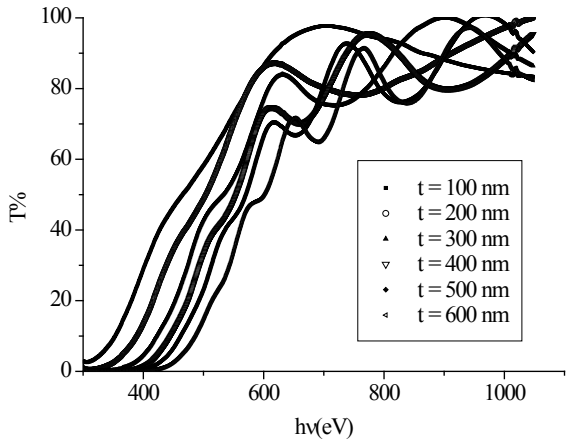

Figure 4. Transmittance of thermally evaporated SnO_2 thin films of different thickness against photon's energy

Fig.5 depicts the relation between $(\alpha h\nu)^{1/2}$ against the photon's energy. A linear fit was performed for each curve and the indirect optical bandgap energy E_{in} was estimated from the intercept with the energy axis with neglecting phonon's energy. The deduced values are inserted in table 2. As the table shows, the indirect optical bandgap energy E_{in} decreases with film thickness. These values are close to the values that we obtained in a previous work[17] for partially polycrystalline SnO_2 thin films prepared by thermal evaporation. On the other hand, these values are smaller than the values given in our previous work[11] for polycrystalline SnO_2:F thin films prepared by the spray pyrolysis technique, the values obtained by Díaz-Flores et. al.[1], the values given by Mohammad and Abdul-Ghafor[18], and those given by Mohammad[19] for spray-deposited SnO_2:F thin films. The reason of this difference is that the optical bandgap increases with doping and our films in this work are not doped.

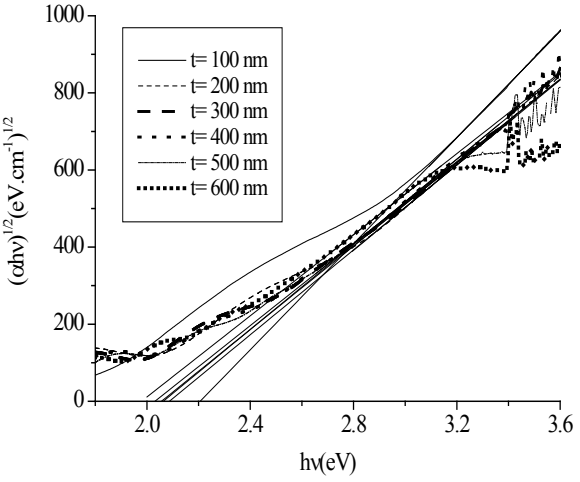

Figure 5. The plot of $(\alpha h\nu)^{1/2}$ against the photon's energy $h\nu$ with the linear fits for amorphous, thermally evaporated SnO_2 thin films of different thickness

It is assumed that in the low photon energy range the spectral dependence of the absorption edge follows the empirical Urbach rule given by[20]

$$\alpha = \alpha_0 \exp(h\nu / E_e) \quad (2)$$

where α_0 is a constant and E_e is the width of the Urbach tail. The exponential tail appears because disordered and amorphous materials produce localized states extended in the bandgap. The absorption edge of these materials at α less than 10^4 cm^{-1}, empirically follows the Urbach law, and this is interpreted as evidence for the existence of localized states. But Urbach law can be applicable to α larger than 10^4 cm^{-1}[20]. To find the width of Urbach tail E_e a plot of $\ln(\alpha)$ against the photon's energy is shown in Fig.6. Linear fits were performed and the values of E_e and α_0 for the whole set of curves were estimated and inserted in table 2.

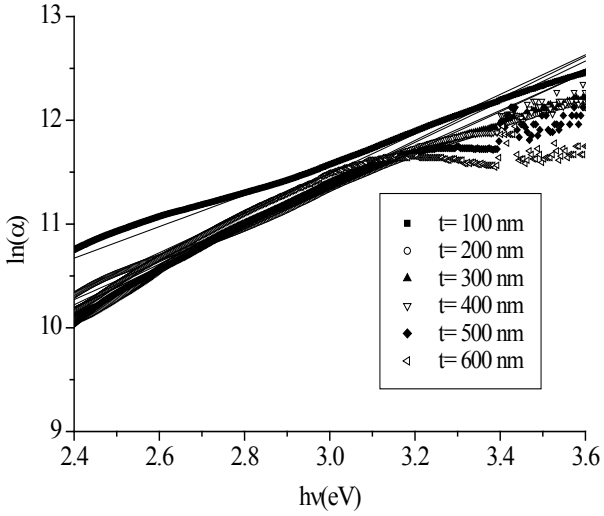

Figure 6. The plot of $\ln(\alpha)$ against the photon's energy $h\nu$ with the linear fits for amorphous, thermally evaporated SnO_2 thin films of different thickness

Table 2. The values of the indirect optical bandgap energy E_{in}, the width of Urbuch tail E_e and the constant α_0 deduced from the linear fits in Figs.4 and 5 respectively beside values of film thickness

t(nm)	α_0(cm^{-1})	E_e(meV)	E_{in}(eV)
100	1.13×10^3	659±2.0	2.21±0.008
200	2.94×10^2	531±1.6	2.09±0.008
300	3.63×10^2	548±1.8	2.02±0.012
400	2.06×10^2	494±0.5	2.06±0.015
500	2.50×10^2	510±1.0	2.03±0.016
600	3.19×10^2	524±1.9	1.98±0.013

Comparing these values with the values that we obtained in ref.[17] for partially polycrystalline SnO_2 thin films prepared by vacuum evaporation, it is found that they are comparable. Also these values are in good agreement with the values obtained by Melsheimer and Ziegler[21] for undoped amorphous SnO_2 thin films prepared by the spray pyrolysis technique which were prepared at deposition temperatures 340 and 350℃. On the other hand these values are larger than the values that we[11] obtained for SnO_2:F thin films prepared by the spray pyrolysis technique and the values obtained by Melsheimer and Ziegler[21] for undoped SnO_2 films which were also prepared by the spray pyrolysis technique at 360-410 ℃ and they are partially

polycrystalline. For these films they[21] got values in the range 350-460 meV. These results confirm that the width of the Urbach tail increases with disorder.

4. Conclusions

Amorphous SnO_2 thin films of thickness in the range 100-600 nm were prepared by thermal evaporation at ambient temperature. X-ray diffractograms showed a wide hump which confirms the amorphous structure of the films. SEM micrographs showed smooth surfaces without features in agreement with the amorphous structures observed by XRD patterns. EDAX analysis revealed that the films are deficient in oxygen which means that they are n-type. The transmittance of the films is very high in the visible and infrared regions. The indirect bandgap and Urbach tail were estimated and related to film thickness. The deduced values are compared with those obtained by different authors.

ACKNOWLEDGEMENTS

I would like to thank Sameer Farrash from the physics department in the University of Jordan for producing the films by thermal evaporation. Also I want to thank Waddah Fares Mahmoud and Azzam Karadsheh from the department of geology in the University of Jordan for taking the SEM micrographs with EDAX analysis and for recording XRD diffractograms, respectively.

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