Effect of Thickness on Optical Dispersion of SnO_2 Thin Films

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Abstract

Highly conducting and transparent SnO_2 thin films have been prepared by a simple and low-cost spray pyrolysis technique on glass substrates. The optical properties and dispersion parameters of tin oxide have been studied as a function of film thickness. The changes in dispersion parameters and Urbach tails were investigated. The optical energy gap Eg decreased with increasing film thicknesses from 200 to 350nm ,and this can be attributed to the increase in the density of localized states and cause an expanding in the Urbach tail and consequently decrease the energy gap from 3.60 eV to 3.49 eV. The single-oscillator parameter has been reported.

Keywords: Dispersion parameters, Spray pyrolysis, Tin Oxide.

تأثير السُمك على عامل التشتت البصري لاغشية اوكسيد القصدير الرقيقة

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الخلاصة

حُضرت اغشية اوكسيد القصدير ذات التوصيلية العالية والشفافة بطريقة التحلل الكيميائي الحراري وهي طريقة بسيطة وواطئة الكلفة . دُرس تأثير سُمك اغشية اوكسيد القصدير على الخصائص البصرية وعوامل التشتت وقد لوحظ وجود تغير في عامل التشتت وذيول اورباخ ، اذ ان فجوة الطاقة البصرية تقل بزيادة سُمك الغشاء من 200nm

الى 350nm . ان زيادة المستويات الموضعية تؤدي الى توسع في ذيول اورباخ وبالتالي تقل فجوة الطاقة من 3.60eV الى 3.49eV .

الكلمات الدالة: التشتت البصري , التحلل الكيميائي , أوكسيد القصدير.

Introduction

SnO_2 is a well-known as transparent conductive oxide, which belongs to the wide-band-gap semiconductor family. It is a promising material for a variety of applications, and seems to be the most appropriate material for different applications in optoelectronic devices such as solar cells, optical filters, high stability resistors, displays and electrochromic devices**,** covering layers for fiber optical systems, photovoltaic devices. Owing to their specific combined electrical, optical and chemical properties have dominated the present scientific world of thin films and gas sensing [1-4]. In addition, they exhibit low electrical resistivity and high optical transmittance.

Various techniques have been applied to study tin dioxide films such as chemical vapor deposition [5], thermal evaporation [6], sol–gel coating [7], laser pulse evaporation [8], magnetron sputtering [9], electron beam evaporation [10] and spray pyrolysis [11]. Among these methods, the spraying technique is a simple, economic and commonly used method and it is well suited for the preparation of tin dioxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [12]. In addition, the tin dioxide prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates.

The current study investigates the optical dispersion characterization of SnO_2 thin films prepared by spray pyrolysis technique. The accurate determination of the optical properties of these films is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications.

Experimental procedure

Thin films of tin oxide have been prepared by chemical pyrolysis technique. The starting solution was achieved by an aqueous solution of 0.1M $SnCl_4.5H_2O$ from Merck chemicals, this material was dissolved in de-ionized water and ethanol, a few drops of HCl were added to make the solution clear, formed the final spray solution and a total volume of 50 ml was used in each deposition. The spraying process was done by using a laboratory designed glass atomizer, which has an output of nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500°C, with the optimized conditions that concern the following parameters, spray time was 7 sec and the spray interval 3 min was kept constant to avoid excessive cooling, the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2}, distance between nozzle and substrate was about 29cm, solution flow rate 5 ml/min. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). In order to explore the influence of film thickness on the parameters under investigation, the films prepared with different thicknesses in the range of 250, 300, 330 and 350 nm.

Results and discussion

The optical properties of SnO_2 thin films by means of optical absorption in the UV to VIS region of (300–900) nm have been investigated. The absorption coefficient (α) could be calculated using the following relation [13]:

$$\alpha = \frac{2.303A}{t} \qquad ....(1)$$

Where (A) is the absorption and (t) is the film thickness. Fig. (1) Shows the dependence of absorption coefficient (α) on the wavelength. The absorption coefficient slightly decreases with the increasing of film thickness. In fact, increasing film thickness could induce a significant deformation of the crystalline state, which suggests modifications in the electronic structure [23]. As a result the decrease in the optical band gap with increasing film thickness can be attributed to the presence of unstructured defects that increase the density of localized states in the band gap and consequently decrease the energy gap such result was also obtained by Shanthi et. al.[14].

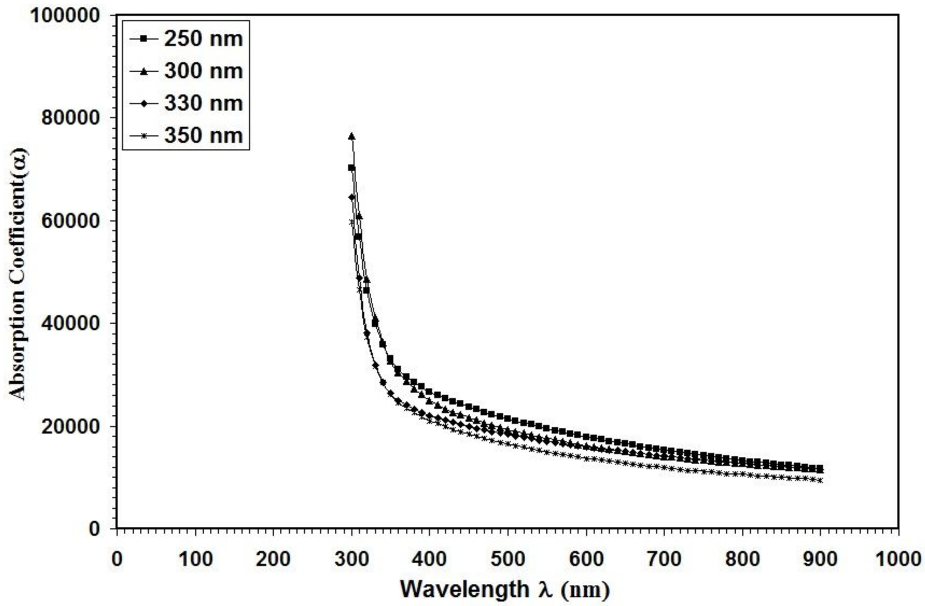

Fig. (1) Absorption coefficient versus wavelength for SnO_2 thin films.

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [15]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [16]:

$\alpha = \alpha^\circ \exp (h\upsilon / E_U)$ ………………… (2)

Where α° is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure (2) shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lnα vs. hυ and is given in Table 1. Increasing film thicknesses change the width of the localized states in the optical band. E_U values change inversely with the optical band gap. The Urbach energy values of the films with thicknesses 200, 250, 300 and 350nm were calculated to be 556, 588, 625 and 667 meV respectively. The increase of E_U suggests that the atomic structural disorder of SnO_2 films increases by increasing films thicknesses. This behavior can result from increasing the concentration of point defects and the formation of solid solutions. So, this increase leads to a redistribution of states, from band to tail. As a result, both a decrease in the optical gap and expanding of the Urbach tail have taken place.

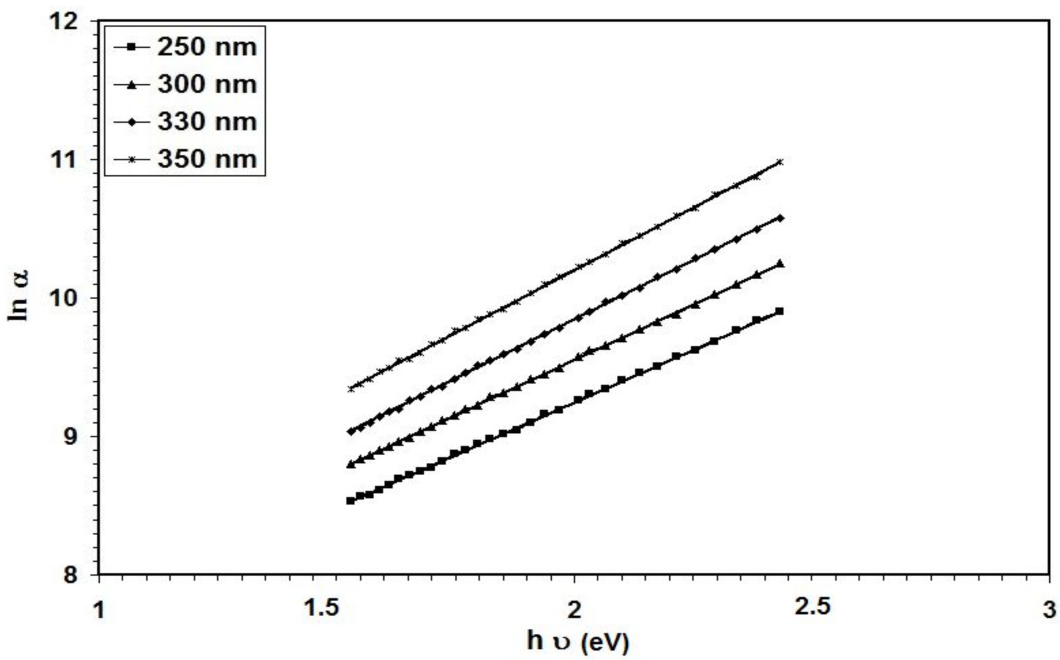

Fig. (2) lnα versus photon energy for SnO_2 films.

The refractive index dispersion plays an important role in optical communication and designing of the optical devices. Therefore, it is important to determine dispersion parameters of the films. The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation [17]:

$$n^2 - 1 = [E_d E_o / E_o^2 - E^2] \quad \text{……….} \ (3)$$

The physical meaning of the single-oscillator energy E_o is that it simulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transitions [18], which is a measure of the intensity of the inter- band optical. This model describes the dielectric response for transitions below the optical gap. $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$ plots for the films was plotted as shown in Fig. (3). E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis and are given in Table 1. E_o values decreased as the optical band gap decreases. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} moments can be derived from the following relations [18]:

$$E_o^2 = M_{-1} / M_{-3} \quad \ldots\ldots\ldots.. (4)$$

$$E_d^2 = M^3_{-1} / M_{-3} \quad \ldots\ldots\ldots (5)$$

The values obtained for the dispersion parameters E_o, E_d, M_{-1} and M_{-3} are listed in Table (1).The obtained M_{-1} and M_{-3} moments changes with the thickness, the results show that both M_{-1} and M_{-3} are increased with increasing the film thickness.

For the definition of the dependence of the refractive index (n) on the light wavelength (λ), the single-term Sellmeier relation can be used [19]:

$$n^2 (\lambda) - 1 = S_o\lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \quad \ldots\ldots\ldots (6)$$

Where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o in Eq. (6) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ against λ^{-2} as shown in Fig. (4), the slope of the resulting straight line gives 1/ S_o, and the infinite-wavelength intercept gives 1/ $S_o \lambda_o^2$. The results shows a decrease in the band gap which may be attributed to the presence of unstructured defects, that increase the density of localized states and cause an expanding in the Urbach tail and consequently decrease the energy gap.

Table (1): The optical parameters

Sample (nm)	E_o (eV)	E_d (eV)	E_g (eV)	E_u meV	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	S_o x10^{13} m^{-2}	λ_o nm
200	7.2	52.72	3.60	556	4.57	2.14	3.57	0.0690	1.44	446
300	7.14	28.57	3.57	588	5.00	2.24	4.00	0.0784	1.67	462
330	7.07	33.67	3.54	625	5.67	2.40	4.76	0.0950	1.84	466
350	6.98	34.92	3.49	667	6.00	2.45	5.00	0.1025	1.97	491

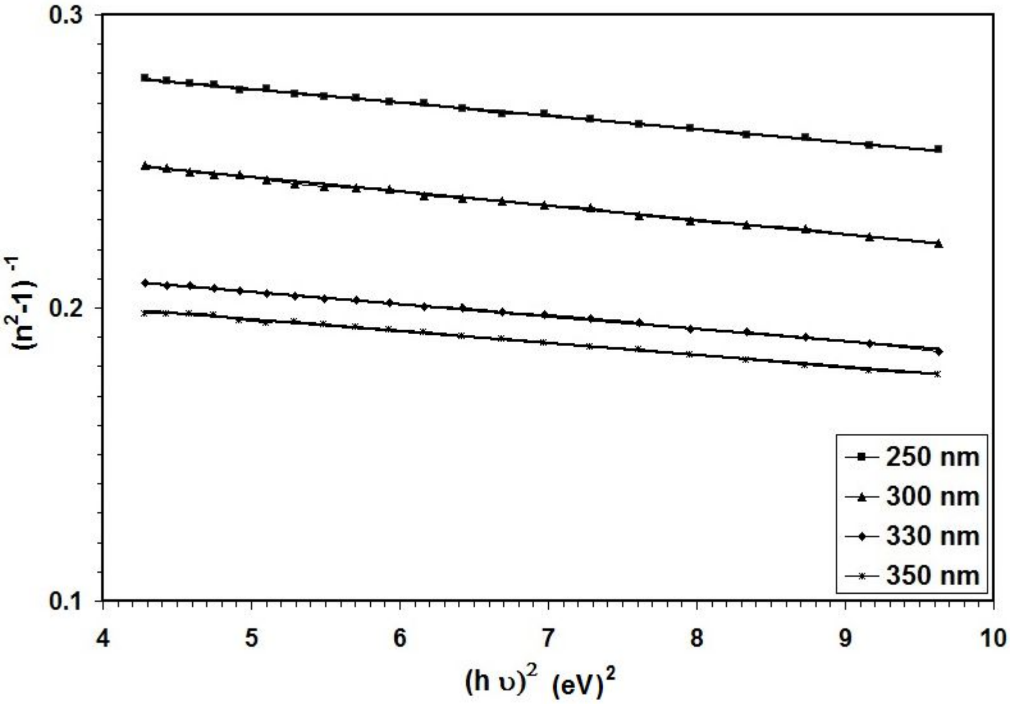

Fig. (3) Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for SnO_2 films.

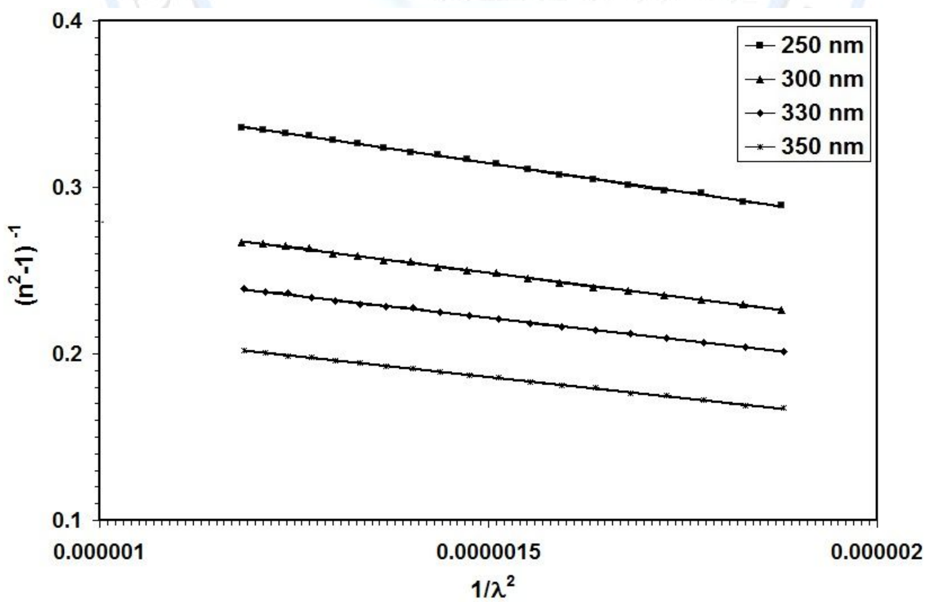

Fig. (4) Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for SnO_2 films.

The optical conductivity was calculated using the relation [20]:

$\sigma = \alpha\, n\, c / 4\pi$ …………….(7)

Where (c) is the velocity of light.

Figure (5) shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity increases with the increasing films thickness to 350nm. It can be noticed from the figure that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region.

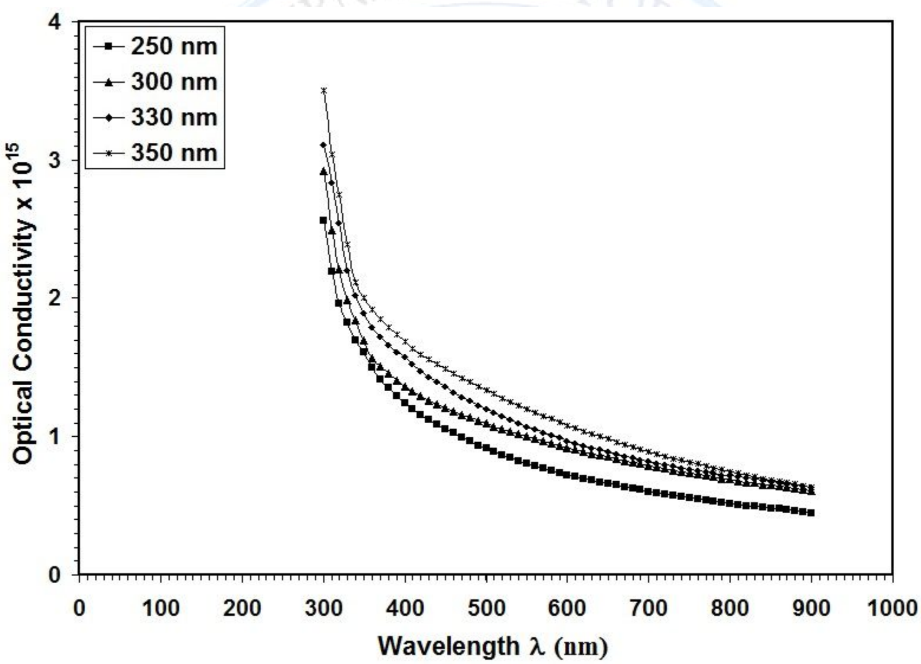

Fig. (5) Optical conductivity versus wavelength for SnO_2 films.

Conclusion

Different thicknesses of SnO_2 thin films were prepared by using spray pyrolysis technique. The optical dispersion parameters were characterized. The optical band gap decreased with increasing film thicknesses. The single–oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value decreased from 7.2 to 6.98 with increasing the film thickness from 200 to 350nm.

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