Thickness Effect on the Electronic Transitions of SnO_2 Films

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Abstract

The authors investigated the effect of thickness on the optical properties of thin films of tin dioxide (SnO_2) fabricated by the chemical spray pyrolysis technique on glass substrates. Optical measurements were studied in the wavelength ranges 300-900 nm. The optical energy gap decreased from 3.7 to 3.5 eV as the film thickness increases from 250 to 350 nm.

Keywords: Transparent conducting oxide (TCO), Optical energy gap, chemical Spray pyrolysis, SnO_2.

Introduction

Transparent conductive films of tin dioxide SnO_2 have a variety of applications in optoelectronic devices such as optical filters, solar cells, high stability resistors, display devices, photovoltaic devices, and switches, owing to their specific combined electrical, optical and chemical properties has dominated the present scientific world of thin films and gas sensing[1-6]. Among the TCOs films, tin dioxide seems to be the most appropriate material for different applications, which is chemically inert, mechanically hard and heat-resistant. In addition, they exhibit low electrical resistivity and high optical transmittance. Furthermore, tin dioxide films are more stable than the other TCOs films such as zinc oxide (ZnO) [7–9]. Moreover, they have a lower material cost.

Currently, a large number of techniques are used to prepare tin dioxide films. These include chemical vapor deposition [10,11], canon-ray evaporation [12], sol–gel coating [13], laser pulse evaporation [14,15], magnetron sputtering [16-20], electron beam evaporation [21,22] and spray pyrolysis [23-25]. 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 [26,27].

In addition, the tin oxide prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates. The crystal structure, composition, electrical conductivity and optoelectronic properties of SnO_2 films depend critically on substrate temperature, preheating rate of deposition, spraying solution, design of the apparatus for spraying, etc. When the extraneous impurities are added to the SnO_2 lattice, the electrical conductivity and optical transparency of SnO_2 films are increased without altering either the transparency or stability of the films [28,29]. The current study investigated the characteristics of SnO_2 thin films by using the spray pyrolysis technique. The optical properties of the films were examined in association with the increase in film thickness.

Experimental details

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 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 the 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 thickness in the range of 250, 300, 330 and 350 nm.

Results and discussion

Information concerning optical transmittance is important in evaluating the optical performance of conductive oxide films. Transmittance spectra in the UV-VIS regions of the films are shown in Fig. 1. Analysis of transmission spectra of SnO_2 films shows that the transmittance of all films increased as the wavelength increase and a general decrease in the transmittance is observed as the film thickness increase. It can be noticed from the figure that increasing film thickness reducing their transparency from 78% to 60%. Such a behavior of transmission coefficient could be explained by specific transformations of defect subsystem during SnO_2 film deposition. Band gap estimations made from the spectral dependence of the transmission coefficient gives values which corresponds quite well with SnO_2 data, published in different sources [30,31].

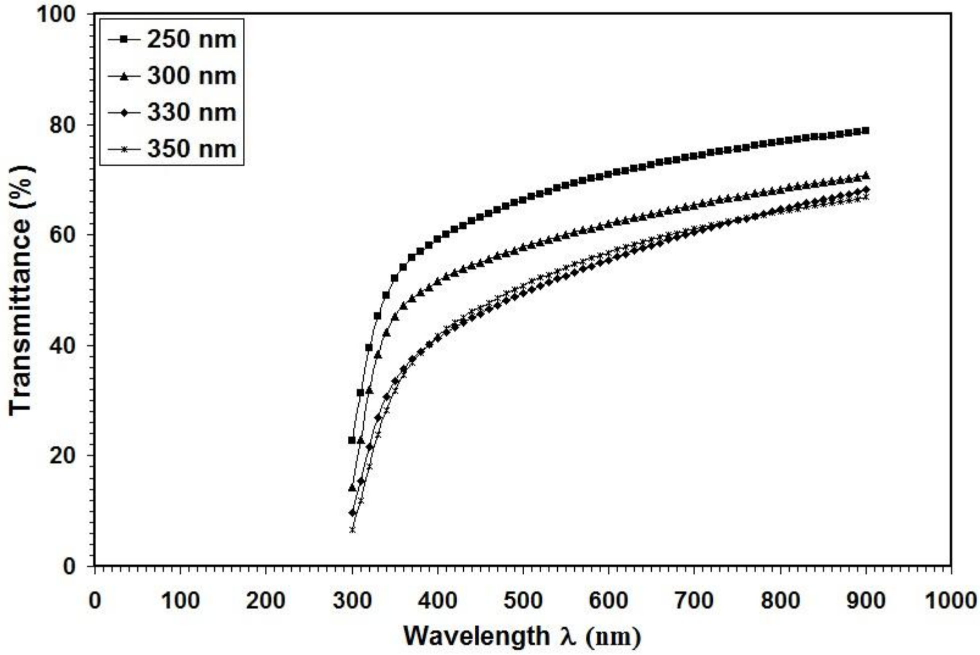

Fig. (1): Transmittance versus wavelength.

Fig. (2) Shows that in the visible region, the reflectance values were observed between 0.1% and 0.2%. The reflectance of all films had a common tendency that the values decreased with the increase in the wavelength. It is seen that the reflectance is limited only by the surface reflectance of about 20% in the visible region. These results were in a good agreement with that obtained by Hong et al. [32].

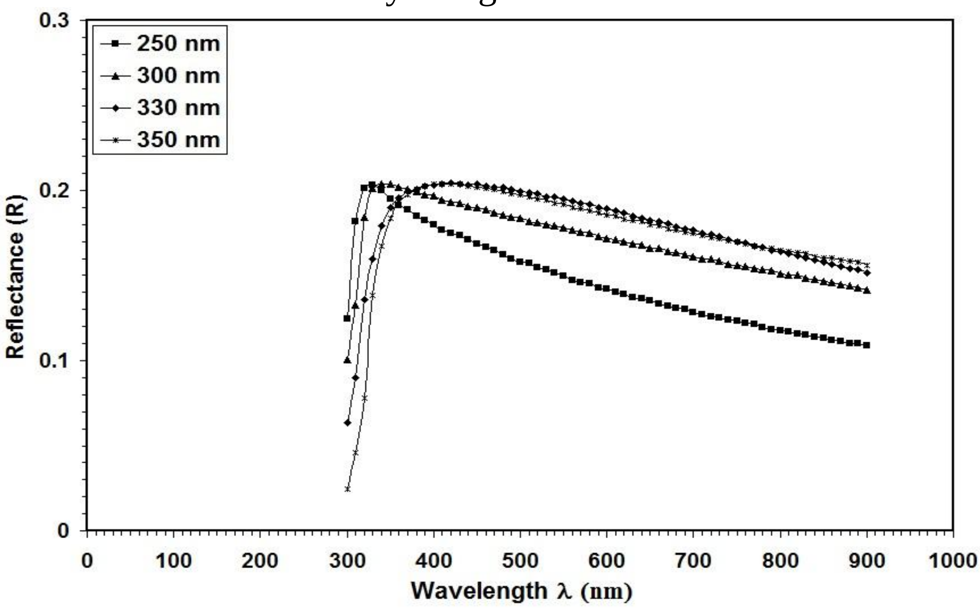

Fig. (2): Reflectance versus wavelength

In order to calculate the band gap of SnO_2 films, we used the Tauc's relationship [33] as follows:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)^n \qquad \ldots\ldots\ldots\ldots(1)$$

where α is the absorption coefficient, A a constant, h is Planck's constant, υ the photon frequency, E_g the optical band gap and n is an index which could take different values according to the electronic transition. An extrapolation of the linear region of a curve of $(\alpha h\upsilon)^2$ on the y-axis against the photon energy (hυ) on the x-axis gives the value of the band gap E_g. According to the absorption spectra measured, $(\alpha h\upsilon)^2$ versus hυ curves of SnO_2 films were plotted and the band gap values were evaluated. Figures 3-6 shows the dependence of the band gap values on the film thickness. Band gap values of 3.7, 3.68, 3.54 and 3.5 eV were obtained for films with thicknesses 250, 300, 330, and 350 nm respectively. It can be seen that the energy band gap of the films tends to decrease with the increase of film thickness. This variation could be assigned to metal particles that induced defects located on the surface of the SnO_2 crystallites. In fact the optical band gap is controlled by the degree of lattice structural and thermal disorder of samples. Carreno et al. [34] showed that amorphous films present a lower band gap compared to crystalline ones. In this study increasing the film thickness could induce a significant deformation of the crystalline state, which suggests modifications in the electronic structure [35]. As a result the decrease in the optical band gap with increasing film thickness can be attributed to a decrease in crystallinity disorder of the films. the results were summarized in Table 1.

Table (1) The Energy Gap of SnO_2 versus film thickness.

Thickness (nm)	Energy Gap (eV)
250	3.7
300	3.68
330	3.54
350	3.5

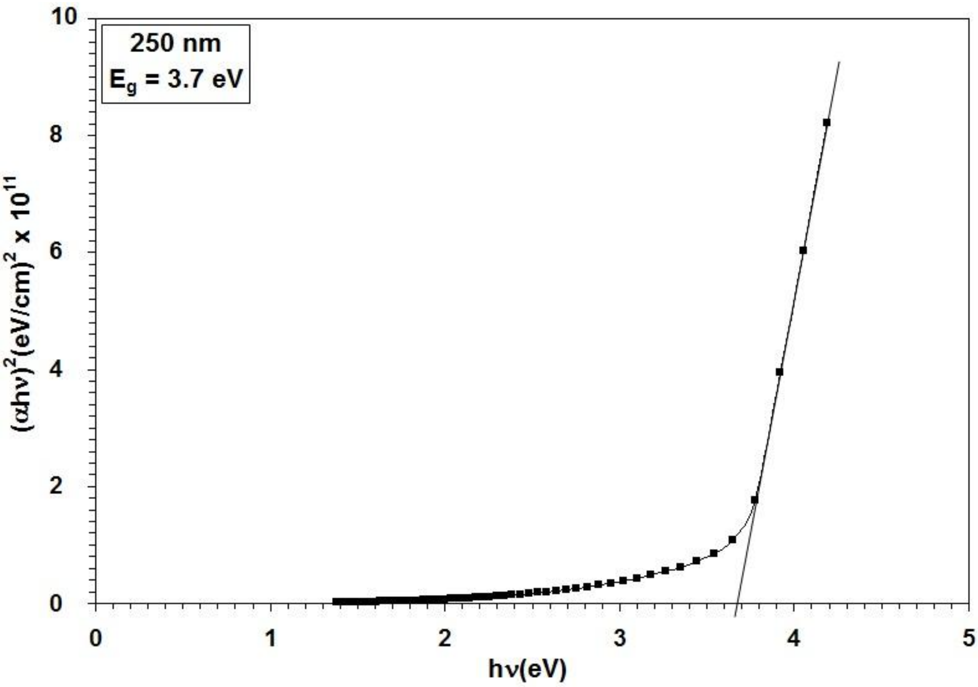

Fig (3) $(\alpha h\upsilon)^2$ for SnO_2 film versus photon energy.

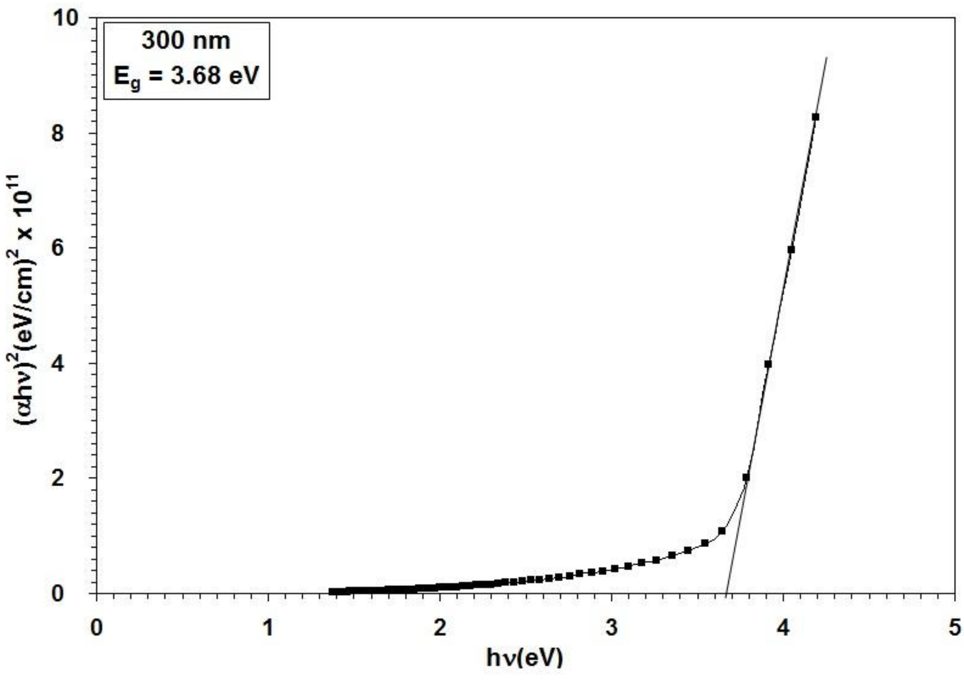

Fig (4) $(\alpha h\upsilon)^2$ for SnO_2 film versus photon energy.

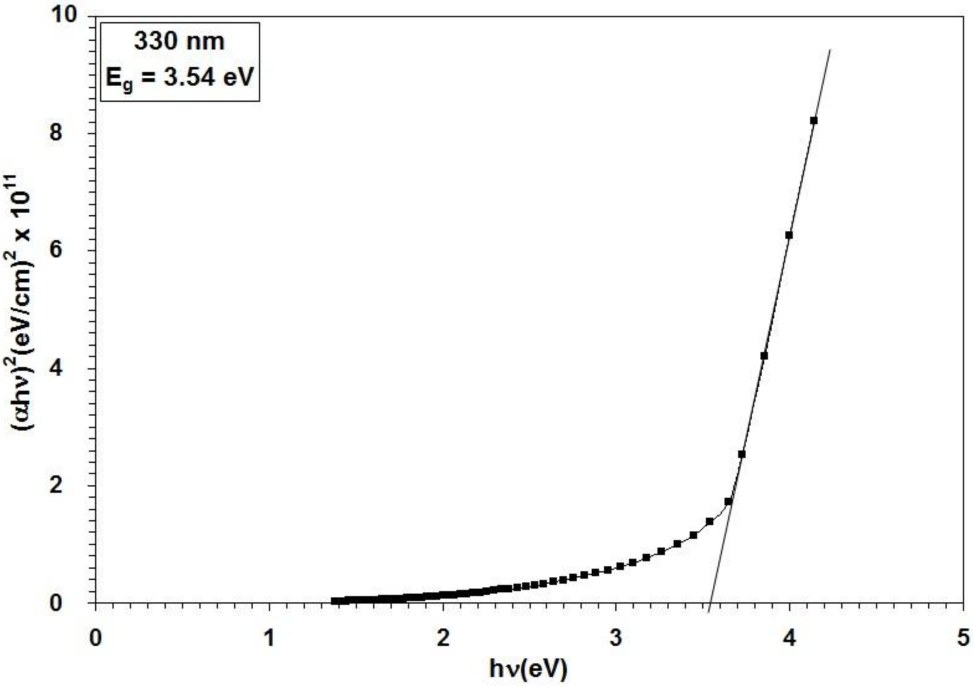

Fig (5) $(\alpha h\upsilon)^2$ for SnO_2 film versus photon energy.

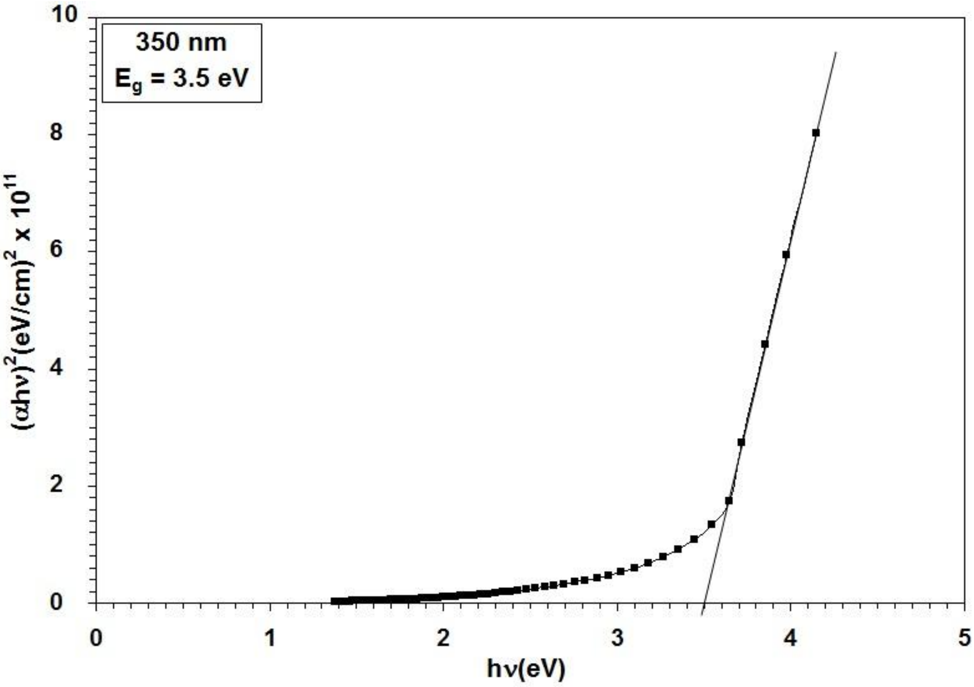

Fig (6) $(\alpha h\upsilon)^2$ for SnO_2 film versus photon energy.

Conclusion

Transparent oxide semiconductor thin films of tin oxide have been successfully deposited onto a glass substrate by the chemical spray pyrolysis technique. All samples were characterized using UV-VIS technique and the results were systematically presented. The optical band gaps were calculated and found to be decreasing with the increasing of film thickness and have the values of 3.7, 3.68, 3.54 and 3.5 eV for the films with thicknesses 250, 300, 330, and 350 nm respectively.

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تأثير السمك على الأنتقالات الألكترونية لأغشية SnO_2

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الخلاصة:

قمنا بتحقيق تأثير السمك على الخصائص البصرية لأغشية (SnO2) الرقيقة المحضرة بواسطة تقنية التحلل الكيميائي الحراري على قواعد زجاجية. تمت دراسة القياسات البصرية الأطوال الموجية 300–900 نانومتر. انخفضت فجوة الطاقة البصرية من 3،7الى 3،5 الكتروت فولت , بزيادة سمك الأغشية 250من الى 350 نانومتر.

الكلمات المفتاحية: أكاسيد التوصيلية الشفافة(TCO), فجوة الطاقة البصرية, التحلل الكيميائي, أوكسيد القصدير.