

**Doping Induced Changes in the Electronic Transitions
of Pure and Sn-Doped ZnO Thin Films**

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Dr. Sami Salman Chiad (*)

Dr. Saad Farhan Oboudi ()**

Dr. Ziad Abdulahad Toma (*)

Dr. Nadir Fadhil Habubi (*)

samichiad2003@yahoo.com, sabodi137@yahoo.com, nadirfadhil@yahoo.com

(*) Al_Mustasiriyah University, College of Education, Physics Department/ Baghdad/ Iraq.

(**) Baghdad University, College of Science, Physics Department/ Baghdad/ Iraq.

Abstract

The un-doped and tin (Sn) doped ZnO films were deposited by spray pyrolysis technique onto glass substrates. 0.1 M solution of zinc acetate in a mixture of ethanol and deionised water. Dopant source was tin chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The atomic percentage of dopant in solution was 2% and 4%. The effect of tin doping on the electronic transitions of ZnO films was studied. The average transmittance values for the films were (76, 84, 88) % for ZnO, ZnO:Sn 2% and ZnO:Sn 4% respectively. The optical band gaps of the films were calculated. The band gap of un-doped sample was 3.36 eV, this value decreased slightly with increasing doping concentration and became 3.17 eV for ZnO:Sn 2% and 3.1 eV for ZnO:Sn 4%.

Keywords: Sn doped ZnO, Spray pyrolysis, transparent conducting oxide (TCO).

Introduction

Transparent conducting oxide (TCO) thin films have been extensively investigated since they constitute a major stage of the production of electronic devices such as semiconducting and laser emitting devices^[1]. Zinc oxide (ZnO) is a direct band gap semiconductor having an energy gap of 3.37 eV at room temperature with high exciton binding energy of 60 meV, which make it a good -candidate has potential applications in various fields such as optoelectronic applications^[2], liquid crystal displays, heat mirrors and multilayer photo-thermal conversion systems^[3] ZnO thin film is also used in the fabrication of solar cells^[4], catalysers^[5], and gas sensors^[6]. In the form of thin film, ZnO is a very promising alternative

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in flat display screens ^[7], compared to tin-doped indium oxides (ITO) which is a limited natural resource. When it is doped, ZnO film presents promising second-order nonlinear optical properties, which achieve the giant nonlinear optical effects about 50 pm/V ^[8,9].

ZnO thin films have been deposited on different substrates by using different techniques such as RF magnetron sputtering ^[10], spray pyrolysis method ^[11], electro-deposition process ^[12], pulsed laser deposition (PLD) ^[13], sol-gel process ^[14], and molecular beam epitaxy ^[15]. Spray pyrolysis, among these methods, is an excellent method for the deposition of thin films of metallic oxides. The doping is achieved by replacing Zn⁺² atoms with atoms of elements of higher valance, such as Al⁺³, In⁺³, Ga⁺³, Sn⁺⁴, Ge⁺⁴, Pb⁺⁴ ^[16].

In this work, un-doped and Sn-doped ZnO (SZO) films have been prepared by using spray pyrolysis technique. The effects of Sn doping concentration on the electronic transitions of ZnO films have been reported.

Experimental details

Thin films of zinc oxide have been prepared by chemical pyrolysis method. The spray pyrolysis 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 450°C, the starting solution was achieved by an aqueous solutions of 0.1M zinc acetate dehydrate (Zn (CH₃COO)₂ .2H₂O) provided from Merck company/ Germany and 0.1M SnCl₂.2H₂O from BDH/ England, used as a doping agent with a concentration of 2% and 4%, these materials were dissolve with de-ionized water and ethanol, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 sec and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10⁵ Nm⁻², distance between nozzle and substrate was about 28 ±1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 0.3 μm.

Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-visible spectrophotometer (Shimadzu Company Japan). Optical transmittance and absorbance were reported in order to find the effect of doping on the parameters under investigation.

Results and discussion

Transmittance and reflectance spectra of un-doped and Tin doped ZnO films dependence on the wavelength is shown in Fig. (1) and Fig. (2), the spectral distribution of *T*

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and R measured at nearly normal incidence in the wavelength range 300–900 nm. It could be noted that at longer wavelengths ($\lambda > 400$ nm), all films become transparent and no light is scattered or absorbed as non-absorbing region. From these spectra, the average values of the optical transmission in the visible range (400–800 nm) were estimated. The average transmittance values for the films were 76, 84 and 88% for ZnO, ZnO:Sn 2% and ZnO:Sn 4% respectively.

The inequality ($R + T < 1$) at shorter wavelengths ($\lambda < 400$ nm) known as absorbing region is due to the existence of absorption. The transmittance is over 80% for the visible region. It can be seen that in the visible region, the transmittance is limited only by the surface reflectance of about 7.5%. This result is in good agreement with the results that obtained by Seval et al. [17] and Lee et al. [18] have indicated that the lower transmittance in Sn-doped ZnO films may be due to the increase in the optical scattering caused by rough surface morphology.

The absorption coefficient (α) could be calculated using the following relation [19]:

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

Where (A) is the absorption and (t) is the film thickness.

Fig. (5) Shows the dependence of the absorption coefficient (α) on the photon energy. The absorption coefficient increases with the increasing of the doping concentration of Sn. It can be seen from the figure that the position of the absorption edge slightly changes, this shifting in the absorption edge may be attributed to the difference in carrier concentration [20].

ZnO exhibits allowed direct inter band transitions. Therefore the band gap is determined from:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \dots\dots\dots(2)$$

Where ($h\nu$) is the photon energy, (α) absorption coefficient, and (E_g) is the band gap. By plotting $(\alpha h\nu)^2$ against $h\nu$, the band gap value can be extrapolated from the straight line at $\alpha = 0$. The known value of the ZnO band gap is $E_g \approx 3.37$ eV [21], therefore E_g deduced from optical measurements is broader than the optical band gap of ZnO. This discrepancy is related to the films surface roughness. Figures (4-6) shows that the Band gap of un-doped sample was 3.36 eV. This decreased slightly with increasing doping concentration and became 3.17 eV for ZnO: Sn 2% and 3.1eV for ZnO:Sn 4%. The band gap could not be exactly inferred from the measured spectra due to scattering nature of the films [22]. The discrepancy encountered may be discussed in terms of film's surface roughness. Filinski [23] has shown that the absorption coefficient α_{ef} deduced from the experimental measurement of the transmission and the reflection spectra is:

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$$\alpha_{ef} = \alpha_o + \alpha_{sc} \dots\dots\dots(3)$$

Where α_o is the absorption of a smooth sample and α_{sc} is the false absorption coefficient related to the scattering of light by the roughness of the surface. Therefore, the scattering of incident light can explain the difference between the expected band gap value and that estimated from experimental measurements^[24].

The incorporation of Tin is accompanied by a systematic low-energy shift of the band gap extending down to the yellow spectral range. The narrowing band gap energy is possibly due to the existence of Tin impurities in the ZnO structure, which induce the formation of new recombination centers with lower emission energy. The optical band gap of Sn-doped ZnO is red-shifted from 3.36 eV to 3.1 eV as the doping weight percentage is increased to 4%. The redshift of the optical band gap is due to the deep states in the band gap and also due to the increasing carrier concentration with Sn doping^[25, 26].

Conclusion

Transparent oxide semiconductor thin films of zinc oxide and tin-doped zinc oxide have been successfully prepared onto glass substrate by the chemical spray pyrolysis technique. Both doped and un-doped samples were characterized using UV-VIS technique and the results were systematically presented. The average optical transmittance, optical band gaps were calculated. The optical band gap of Sn-doped ZnO is red-shifted from 3.36 to 3.1 eV as the doping weight percentage is increased to 4%. The redshift of the optical band gap is due to the deep states in the band gap. It is supposed that tin atoms occupying Zn site and/or at interstitial position might be the major reason for decreasing the optical energy gap of doped samples. Similarly optical transmittance was affected for moderate doping. Both ZnO and Tin doped ZnO show high transmittance in the visible range and exhibit sharp adsorption edge in the ultraviolet. Such modification of the transmission properties of the film testifies of the presence of a high concentration of mobile electrons in the crystallites of the film.

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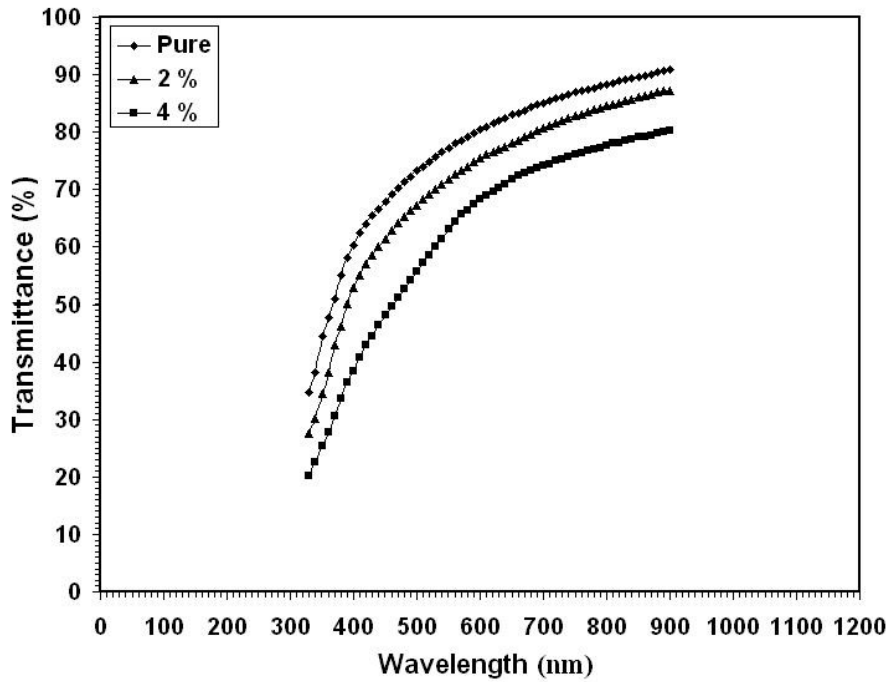


Fig. (1) Transmission of ZnO and ZnO:Sn thin films versus wavelength.

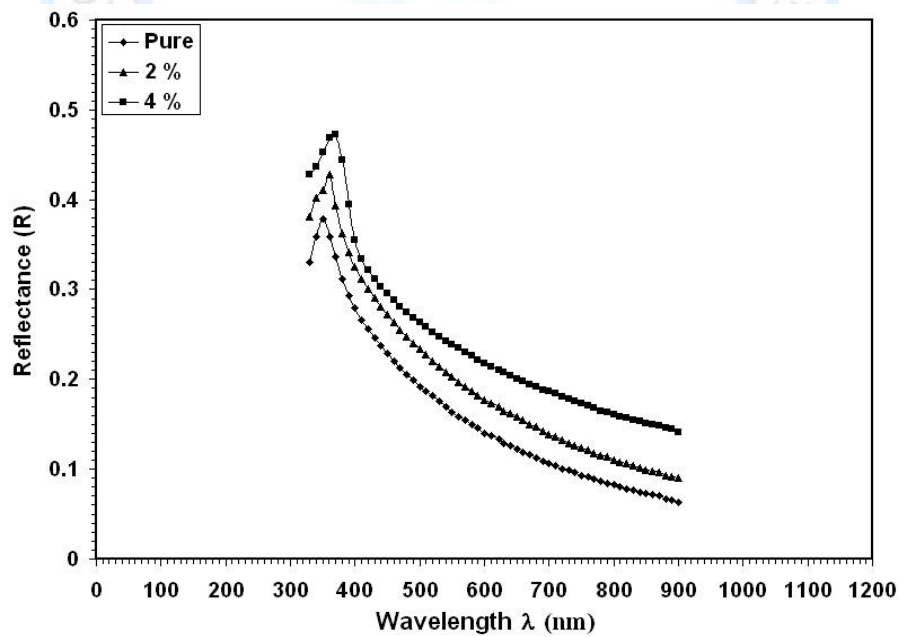


Fig. (2) Reflectance of ZnO and ZnO:Sn thin films versus wavelength.

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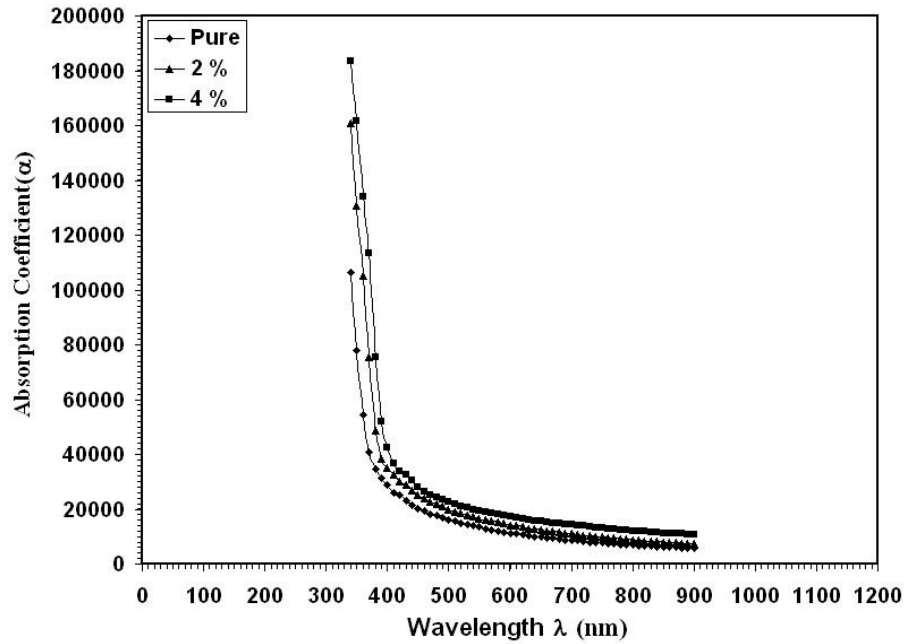
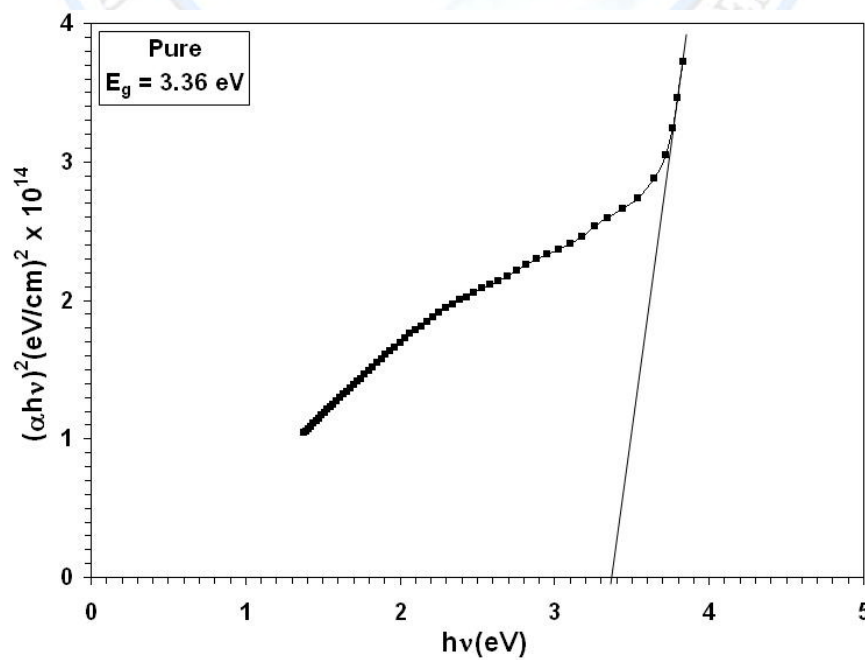


Fig. (3) Absorption coefficient versus wavelength of ZnO and ZnO:Sn thin films.



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Fig (4) $(\alpha h\nu)^2$ for un-doped ZnO thin films versus photon energy.

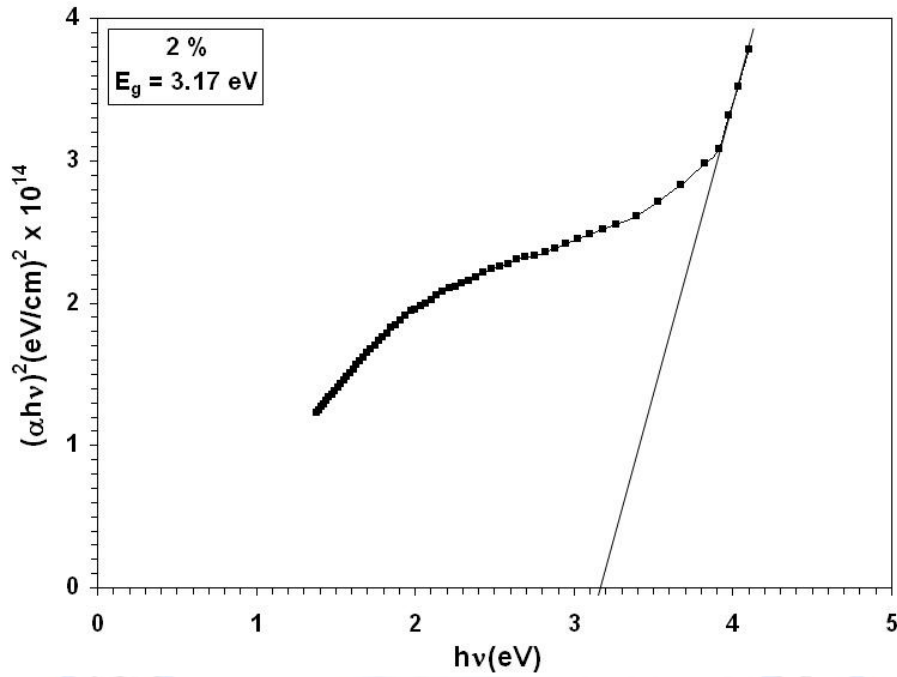
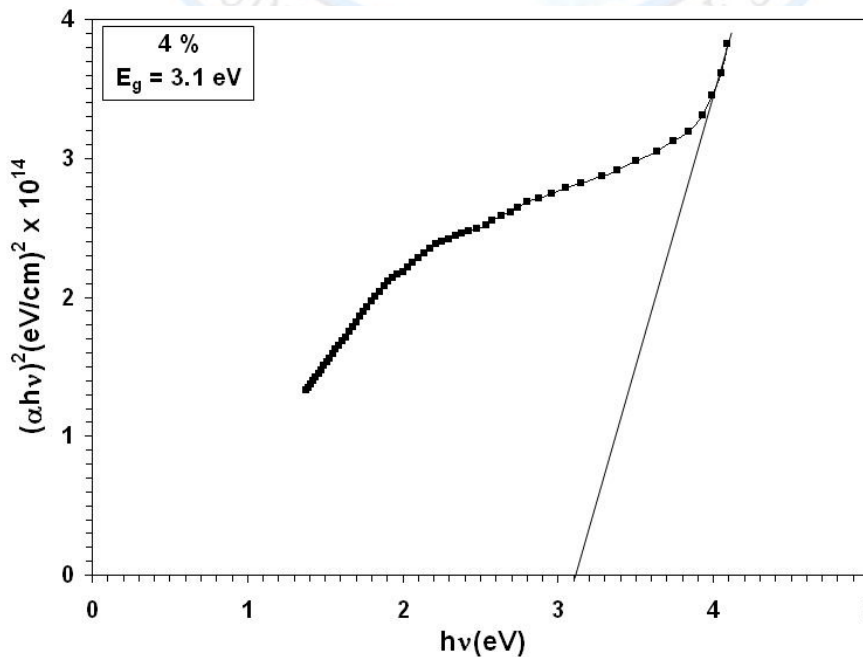


Fig (5) $(\alpha h\nu)^2$ for ZnO:2%Sn thin film versus photon energy.



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Fig (6) $(\alpha h\nu)^2$ for ZnO:4%Sn thin film versus photon energy.

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**التغيرات الناجمة عن التشويب في الانتقالات الالكترونية
لأغشية أكسيد الخارصين الرقيقة النقية والمشوبة بالقصدير**

د. سامي سلمان جواد*، د. سعد فرحان العبودي**، د. زياد عبد الاحد توما*،

د. نادر فاضل حبوبى*

* الجامعة المستنصرية – كلية التربية – قسم الفيزياء- بغداد- العراق

** جامعة بغداد – كلية العلوم – قسم الفيزياء- بغداد- العراق

الخلاصة

تم ترسيب أغشية رقيقة من أكسيد الخارصين وأكسيد الخارصين المشوب بالقصدير على قواعد زجاجية باستخدام تقنية التحلل الكيميائي الحراري. حضر 0.1M من محلول اسيتات الخارصين مع خليط من الماء المقطر والايثانول ، اما مصدر القصدير فقد كان $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. تم دراسة تأثير نسب التشويب 2% و 4% من القصدير Sn على الانتقالات الالكترونية وفجوة الطاقه البصريه لأغشية ZnO، أن معدل قيم الامتصاصيه للأغشيه المحضره كانت (76, 84, 88) للأغشيه النقيه والمشوبه بالقصدير بنسبة 2% و 4% على التوالي. تم حساب فجوة الطاقه البصريه للأغشيه الرقيقه حيث وجدنا أن فجوة الطاقه للأغشيه النقيه $E_g = 3.36 \text{ eV}$ تقل هذه القيمه لتصبح 3.17 eV و 3.1 eV للأغشيه المشوبه بالقصدير بنسبة 2% و 4%.

الكلمات المفتاحية : أكسيد الخارصين مشوب بالقصدير، التحلل الحراري ، الأكاسيد الموصلة الشفافة.