Influence of dopant concentration on Dispersion Parameters of ZnO:Sn Thin Films

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Abstract

Undoped and Sn doped ZnO films have been deposited by spray pyrolysis technique. The films were deposited onto glass substrate at a temperature of 450°C. The effect of tin incorporation on optical properties and dispersion parameters of ZnO films has been investigated. Optical absorption measurements were also studied by UV-VIS technique in the wavelength range 300-900 nm. The optical band gap of these films was determined. The absorption edge shifted to the lower energy depending on the dopant materials. The changes in dispersion parameters and Urbach tails were investigated as a function of Sn content. The optical energy gap decreased and the wide band tails increased in width from 442 to 546 meV as the doping concentration increased from 0wt.% to 4wt.%. The single–oscillator parameters were determined.

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تأثيـــر التشويب على معلمـــــات التفريق لأغشية ZnO:Sn الرقيقـــــة

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الخلاصة

تم دراسة أغشية أوكسيد الزنك النقية ZnO والمشوبه بالقصدير ZnO:Sn بواسطة تقنية التحلل الكيميائي الحراري، تم ترسيب الأغشية على قواعد من الزجاج بدرجة حراره 450 °C. درست أيضا القياسات البصرية حيث سجل طيف الامتصاصية في مدى الأطوال الموجية (٣٠٠- ٩٠٠) نانومتر لحساب الثوابت الضوئية. وقد تم التحقق من التغيرات في معلمات التفريق وطاقة أورباخ بزيادة نسبة التشويب بالقصدير Sn. انخفضت فجوة الطاقة الضوئية بينما ازداد نطاق عرض الذيول من ٤٤٢-٥٤٦ ملي الكترون فولت بزيادة محتوى Sn من 0wt.% الى 4wt.%. كذلك تم حساب طاقة المتذبذب المفردة في معلمات التفريق قبل وبعد التشويب.

Keywords: Spray pyrolysis, transparent conducting, ZnO, Dispersion Parameters.

Introduction

ZnO is an important wide-band-gap semiconductor (E_g=3.37 eV) that has a direct band-gap with a high exciton binding energy (60 meV), which is greater than the thermal energy at room temperature. It is a promising material for ultraviolet nano-optoelectronic devices and lasers operating at room temperature [1]. As is well known, impurity-doping in semiconductors with selective elements greatly affects the basic physical properties, such as the electrical, optical, and magnetic properties, which are crucial for their practical application such as photovoltaic devices and optical–electrical devices. Among these materials, zinc

oxide (ZnO) is a promising transparent oxide that has been extensively used for candidate for novel device applications, such as transparent electronics [2, 3] and flexible displays [4, 5].

Usually, selective elements as dopant materials in ZnO can be classified into two groups of materials. One group can substitute for Zn and the other can substitute for O. These different types of doping materials can exhibit different optical properties for ZnO due to the different treatments of Zn and O in the ZnO structure. Each exhibits very different behavior as dopant material in ZnO nanostructures [6]. Sn as a cation dopant can substitute for Zn. It can be applied as an impurity that changes the band-gap of ZnO. By alloying ZnO with another material of a different band-gap, the band-gap of ZnO can be fine-tuned.

Whereby, the doping of ZnO with $SnCl_2.2H_2O$ creates a ZnO/ $SnCl_2$ structure, a potential candidate for future optoelectronic devices, since the addition of Sn results in reduces the band gap. This reducing of the gap is due to the ionized donor [7]. Various techniques have been applied to study Sn-doping including RF magnetron sputtering, spray pyrolysis method, electro-deposition process, chemical vapor deposition, metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), sol-gel process, and molecular beam epitaxy [8-15]. In this work, un-doped and Sn-doped ZnO films have been prepared by using the spray pyrolysis technique.

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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 ($Zn(CH_3COO)_2.2H_2O$) provided from Merck company/Germany and 0.1M $SnCl_2.2H_2O$ 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 ٨ sec and the spray interval (٢min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2}, distance between nozzle and substrate was about 28 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 (300-900nm) 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 discussions

The optical properties of un-doped ZnO and ZnO:Sn thin films by means of optical absorption in the UV to Vis region of (300–900) nm have been investigated. From the absorption spectra of un-doped sample, it was clear that there was almost no absorption in the visible region. But for the doped samples, absorption edge was not sharp and there was absorption in this region Fig. (1). This might be due to the introduction of shallow donor level due to doping of Sn. Slight shift in absorption edge towards the higher wavelength for the doped sample was also clear from the absorption spectra. This result was in good agreement with the results obtained by Aranovich et al. [16].

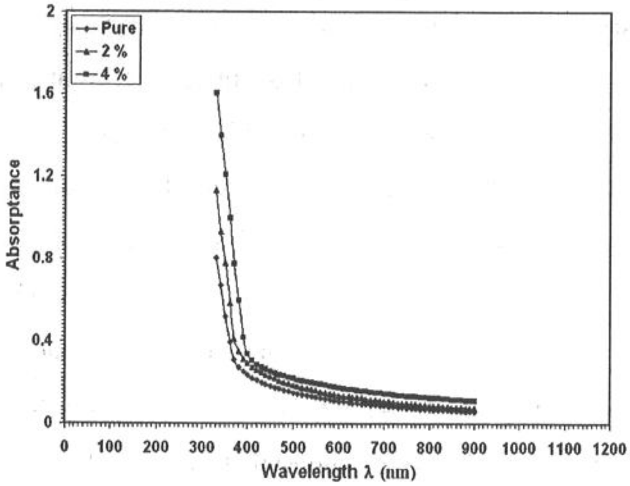

Fig. (1) Absorptance of ZnO and ZnO:Sn thin films versus wavelengths

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The incorporation of impurity into the semiconductor often reveals the formation of band tailing in the band gap. 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 [18]. 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 [19]

$$\alpha = \alpha^\circ \exp (h\upsilon / E_U) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where α° is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Equation (1) describes the optical transition between the occupied states in the valence band tail to the unoccupied states of the conduction band edge. Figure (2) shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of $\ln\alpha$ vs. $h\nu$ and is given in Table 1. The dopants change the width of the localized states in the optical band. E_U values change inversely with optical band gap. The Urbach energy values of ZnO, ZnO:Sn2%, and ZnO:Sn4% films were calculated to be 442, 532, and 546 meV respectively. The increase of E_U suggests that the atomic structural disorder of ZnO films increase by tin doping. This behavior can result from the increasing concentration of point defects induced by the dissolution of Sn in ZnO crystals and formation of solid solution. So, this increase leads to a redistribution of states, from band to tail, thus allowing for a greater number of

possible bands to tail and tail to tail transitions [20]. As a result, both a decrease in the optical gap and a broadening of the Urbach tail are taken place.

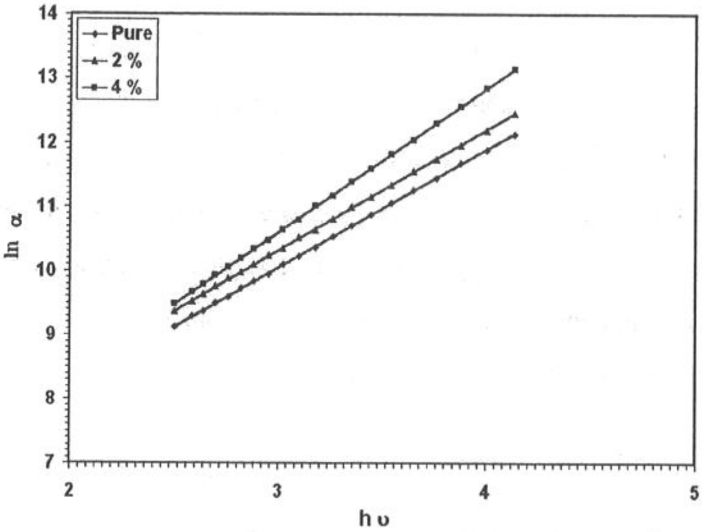

Fig. (2) lnα versus photon energy.

The refractive index dispersion plays an important role in optical communication and designing of the optical devices. S_o, 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 [21, 22]:

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

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 [23], 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. $(hv)^2$ 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 with the dopants as optical band gap. The refractive index dispersion curves show that the films obey the single oscillator model. 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 [24] can be derived from the following relations:

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

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

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 dopants.

For the definition of the dependence of the refractive index n on the light wavelength (λ), the single-term Sellmeier relation can be used [21]:

$$n^2(\lambda) - 1 = S_o.\lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \quad \ldots\ldots\ldots\ldots (4)$$

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. (4) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ against λ^{-2} as shown in figure 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 band gap which may 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 [25-27].

Table (1) the optical parameters

Sample	E_o (eV)	E_d (eV)	E_g (eV)	ε_∞	n(o)	M_1 eV^{-2}	M_3 eV^{-2}	S_o x10^{13} m^{-2}	□$_o$. nm	E_U (meV)
Pure	6.495	24.056	3.248	4.704	2.169	3.704	0.0878	5.028	464	442
2 %	6.156	24.618	3.077	5.000	2.236	4.000	0.1056	7.205	427	532
4 %	5.859	25.474	2.923	5.348	2.313	4.348	0.1267	14.402	388	546

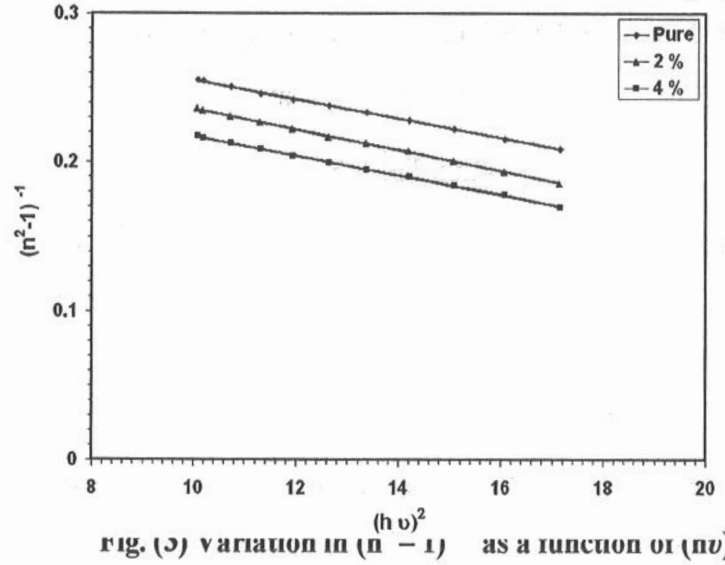

Fig. (5) Variation in $(n^2-1)^{-1}$ as a function of $(h\upsilon)^2$ of ZnO and ZnO:Sn films.

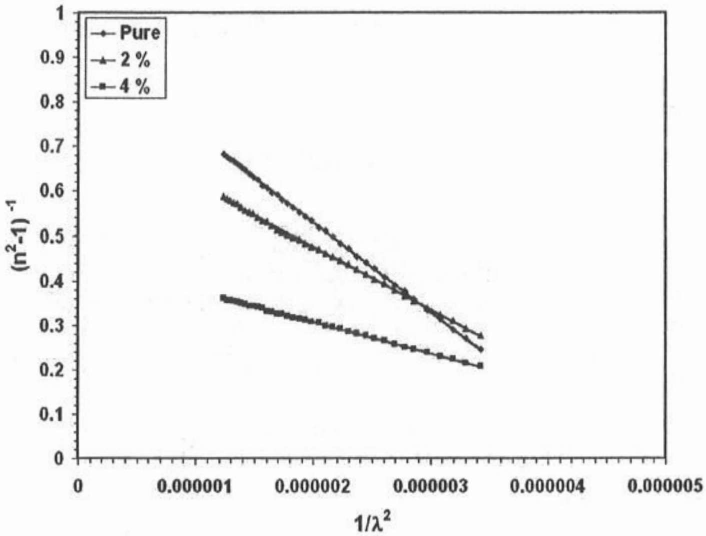

Fig. (4) Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ of ZnO and ZnO:Sn films.

Conclusions

Un-doped and Sn doped ZnO films were deposited onto glass substrate by spray pyrolysis at a temperature of 450 C. Absorbance spectra were used to determine the optical constants of the films, The values of the direct band gap E_g decreased with increasing the doping percentage of Sn to 4wt.%.

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 before and after doping and its value increased from 13.35 for the un-doped films to 25.90 for the doped films with 4wt.% of Sn.

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