Effect of Ga Doping Concentration on the Inter-Band Transitions of ZnO Thin Films

Dr. Ziad Abdulahad Toma

ziad_a_toma@yahoo.com

,Al_ Mustansiriyah University, College of Education, Physics Department

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Abstract

Gallium-doped ZnO (GZO) semiconductor thin films were deposited onto glass substrates using the spray pyrolysis technique. The effect of Ga dopant concentration on the optical properties of ZnO thin films was studied. ZnO thin films doped with Ga has been improved optical transmittance in the visible region

تاثيرتركيز التشويب بالكاليوم على الانتقالات الحزمية لاغشية اوكسيد الخارصين الرقيقة

د. زياد عبد الاحد توما

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

الخلاصة

حضرت أغشية رقيقة من شبه الموصل (اوكسيد الخارصين المشوب بالكاليوم) على قواعد زجاجية باستعمال تقنية التحلل الكيميائي الحراري . تمت دراسة تاثير تركيز الكاليوم كشائبة على الخواص البصرية لاغشية اوكسيد الخارصين . لقد تبين بان التشويب قد يحسن من النفاذية البصرية في المنطقة المرئية.

Introduction

Transparent conducting oxide (TCO) films have been widely studied for their practical applications as transparent conductive electrodes, window materials in display, window layer in solar cells [1], light emitting devices [2], gas sensors [3], and various optoelectronic and acoustic wave filters devices [4–6]. Intrinsic ZnO is assumed to be an n-type semiconductor mainly because of donor defects such as zinc interstitials (Zn_i) and oxygen vacancies (V_o). Therefore, the treatment of un-doped ZnO described above increases the cation-to-anion ratio of ZnO, resulting in an increase in the conductivity of ZnO. Un-doped nonstoichiometric ZnO thin films have unstable electrical and optical properties [7]. Unlike these nonstoichiometric ZnO films, n-type doped ZnO films show stable electrical and optical properties [8]. 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} [9]. Doping of ZnO using Ga species in particular is more effective for the stabilization of lattice systems and increases the ionicity of chemical bonds in ZnO films.

The important properties of ZnO are due to its wide direct band gap of 3.37 eV [10, 11]. Bulk ZnO is quite expensive and is unavailable in large wafers. So, for the time being, thin films of ZnO are relatively a good choice. Usually, the doped ZnO films with optimum properties i.e. perfect crystallite structure; good conducting properties, high transparency and high intensity of luminescence are obtained when they are grown on heated substrates and annealed after deposition at high temperature in an atmosphere of oxygen. However, for an extensive use in the commercial applications, pure ZnO films must be prepared at much lower substrate temperatures.

Generally, gallium-doped ZnO (ZnO:Ga) films are fabricated by chemical vapor deposition (CVD) [12], magnetron sputtering [13], sol–gel techniques [14], spray pyrolysis [15] and pulsed laser deposition [16]. In this work, transparent conducting ZnO:Ga films deposited on glass substrates by spry pyrolysis technique are reported. The effect of doping concentration on the optical properties of ZnO and ZnO:Ga transparent films are investigated in detail.

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 400°C, the starting solution was achieved by an aqueous solutions of 0.1M Zn $(CH_3COO)_2$. $2H_2O$ from Merck chemicals and 0.1M $GaCl_2$ from BDH chemicals used as a doping agent with a concentration of 2% , 5% and 7%, these materials were dissolved with de-ionized water and ethanol, 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 10^5 Nm^{-2}, distance between nozzle and substrate was about 29 ±1 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 350 nm. 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 study the effect of doping on the parameters under investigation.

Results and discussion

The optical absorption measurements were carried out in the UV/VIS region (300-900 nm) for undoped ZnO films and ZnO doped with different contents of Ga. The transmittance and reflectance of pure and doped ZnO films recorded in the applied wavelength range are shown in Figures 1 and 2. It is clear from these figures that transmittance spectra for all films increase with increasing wavelength from (600-900) nm while reflectance decreased in the same range. Increasing the Ga content of the films decreases transmittance and increases reflectance for a lower wavelength range (300-600) nm. This means that there is some absorption in that wavelength range. For each composition typical spectral behavior of transmittance and reflectance are given for pure and doped ZnO films. Similar behavior was also obtained by Cheong *et al.* [17]. Also, It can be noticed that all the samples exhibit very high transmittance of over 80% over a wide spectral range from (600-900) nm. Such result was confirmed by Tseng et al. [18].

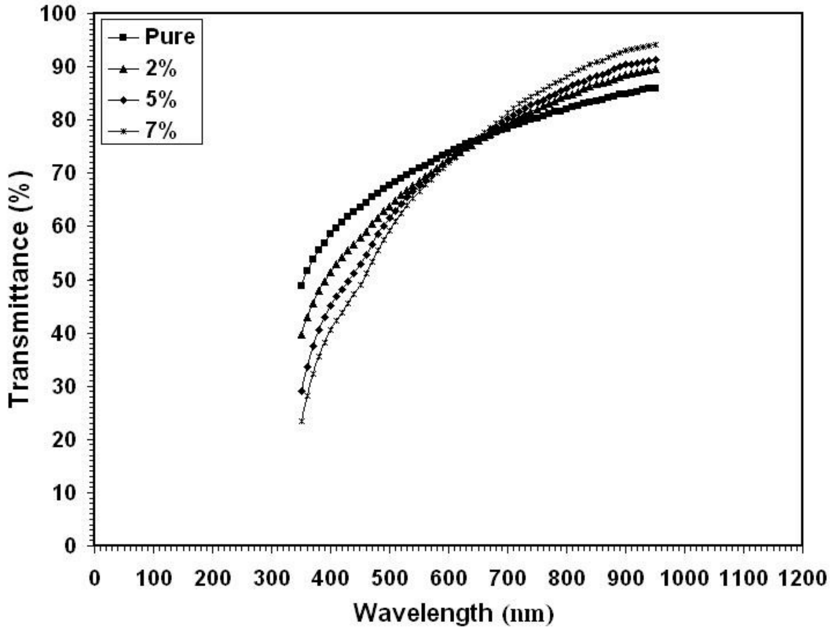


Fig. (1) Transmission of ZnO and ZnO: Ga thin films versus wavelength.

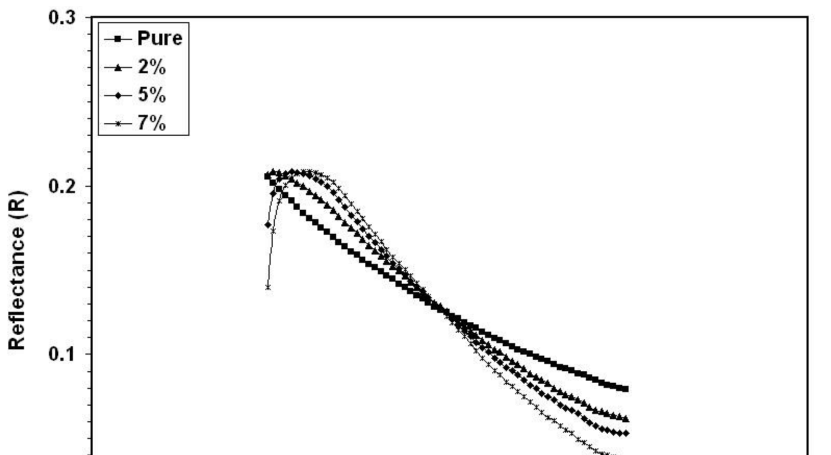


Fig. (2) Reflectance of ZnO and ZnO:Ga thin films versus wavelength.

The UV–VIS absorption spectra in the region (300-900 nm) for ZnO, ZnO:2%Ga, ZnO:5% Ga and ZnO:7% Ga thin films are shown in Fig. (3). The ZnO film shows a sharp absorption edge at about 425 nm. In contrast, the absorption edge of the ZnO:Ga thin films has been slightly shifted to higher wavelengths (red-shifted) to 510 nm. It is clear from the figure that absorption spectra for all films increase with increasing wavelength from (300-600) nm. Increasing the Ga content of the films decreases the absorption for a higher wavelength range (600-900) nm. This means that there is some absorption in that wavelength range. Such result was confirmed by Cheong *et al*. [17] and Tseng *et al*. [18]. It is evident that the optical absorbance increases in the visible region with increasing the doping concentration of Ga.

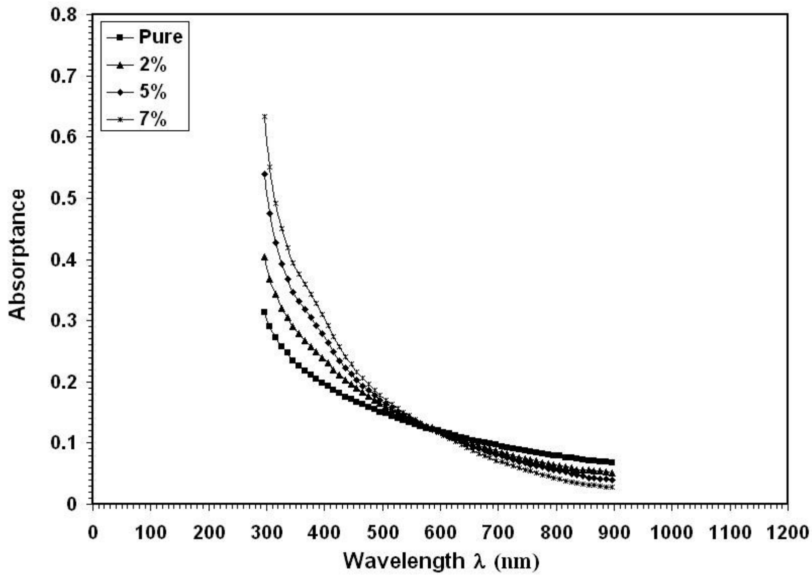


Fig. (3) Absorptance versus wavelength for .the ZnO and ZnO:Ga thin films

The refractive index dispersion plays an important role in the 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]:

$$n^2 - 1 = [E_d E_o / (E_o^2 - E^2)] \quad \dots\dots\dots (2)$$

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. $(h\nu)^2$ plots for the films was plotted as shown in Fig. (4). 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 decrease 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 can be derived from the following relations: [24]

$E_o^2 = M_{-1} / M_{-3}$ ……….. (2)

$E_d^2 = M^3_{-1} / M_{-3}$ ………. (3)

The values obtained for the dispersion parameters E_o, E_d, M_{-1} and M_{-3} are listed in Table (1) (M_{-1} without units).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 [25]:

$n^2(\lambda) - 1 = S_o.\lambda_o^2 / [1 - (\lambda_o/\lambda)^2]$ ………. (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. (5) 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 an increase in band gap which may be attributed to the presence of unstructured defects.

Table (1) the optical parameters

Sample	E_o (eV)	E_d (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	S_o x10^{13} m^{-2}	λ_o nm	lnα
Pure	6.251	19.521	3.12	4.13	2	3.125	0.08	0.983	442	740
2%	6.3	20.34	3.15	4.23	2.06	3.23	0.081	0.599	481	714
5%	6.45	21.52	3.23	4.35	2.08	3.33	0.08	0.480	513	645
7%	6.63	22.86	3.31	4.45	2.11	3.45	0.078	0.335	560	606

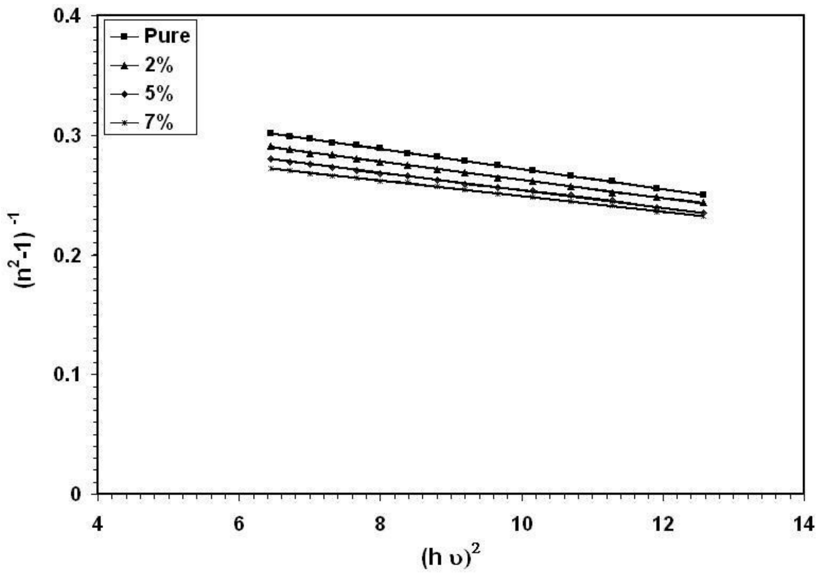


Fig. (4) Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$

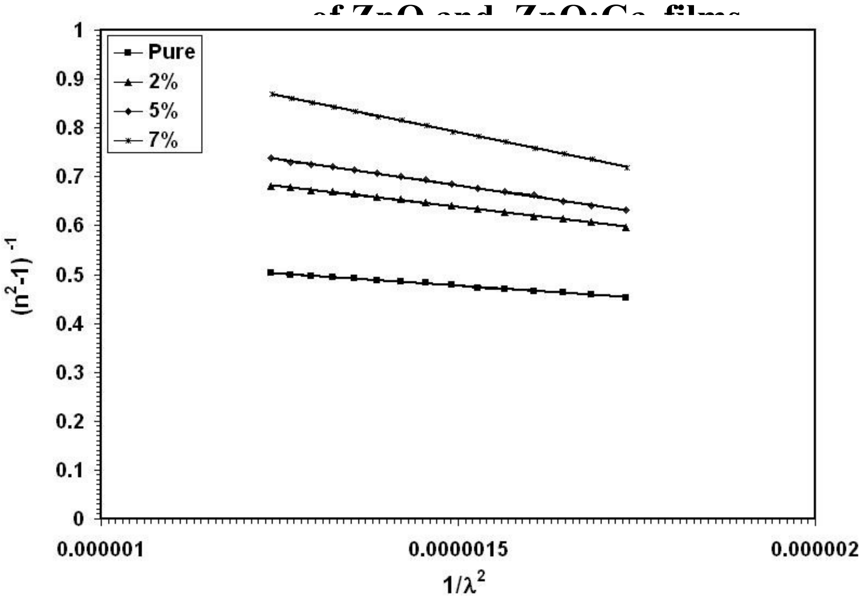
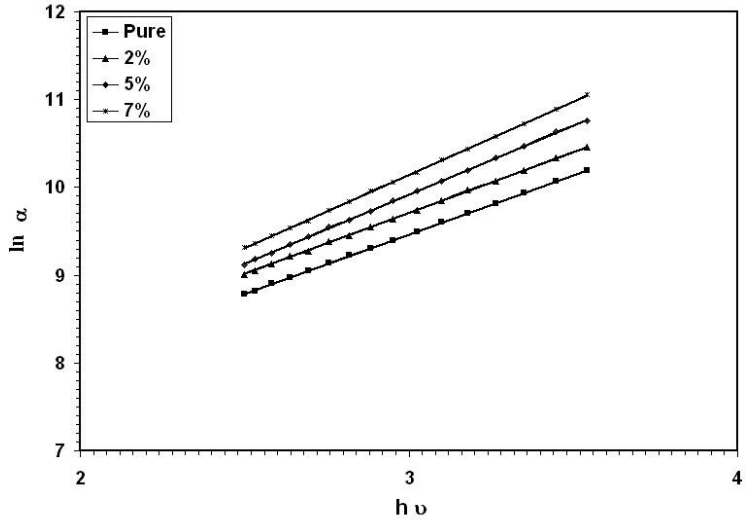


Fig. (5) Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ .of ZnO and ZnO:Ga films

The incorporation of impurity into the semiconductor often reveals the ormation 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 [25]. 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 [26]:

$$\alpha = \alpha^{\circ} \exp\left(h\upsilon \triangleleft E_U\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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 (6) shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lnα vs. hν 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 and ZnO doped Ga films were found to be decreased which leads to an increase in the energy gap. This behavior can result from the increasing concentration of point defects induced by the dissolution of Ga in ZnO crystals and formation of solid solution. So, this increase leads to a redistribution of states, from band to tail, thus allowing a greater number of possible bands to tail and tail to tail transitions [27]. As a result, both an increase in the optical gap and a narrowing of the Urbach tail are taken place.



.Fig. (6) lnα versus photon energy

The optical conductivity was calculated using the relation [21]:

$$\sigma = \frac{\alpha\, n\, c}{4\, \pi} \quad \text{...............} \ (5)$$

Where c is the velocity of light.

Figure (7) shows the variation of optical conductivity with the wavelength, the conductivity values of the ZnO and ZnO: Ga films at room temperature. It was observed that the optical conductivity increases as the percentage of Ga in the ZnO increases to 7%. The increased optical conductivity at high photon energies is due to the high absorbance of the films in that region.

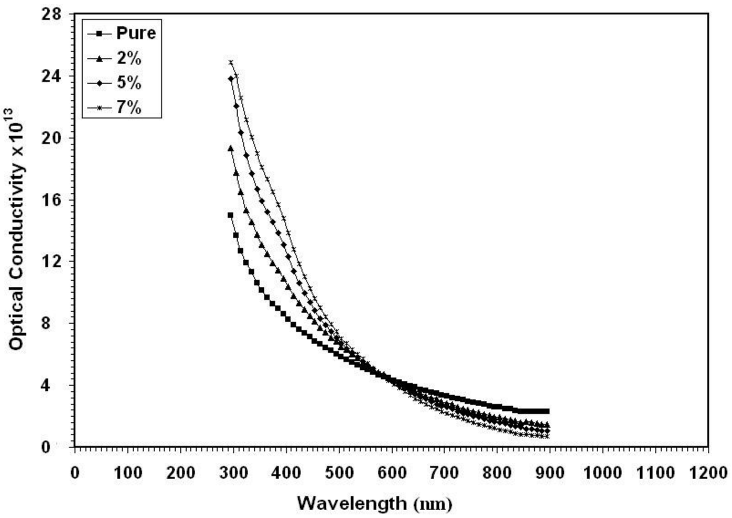


Fig. (7) Optical conductivity versus wavelength
.for the ZnO and ZnO:Ga films

Conclusion

ZnO and gallium doped ZnO films were prepared by using the chemical spray pyrolysis technique. Both doped and un-doped samples were characterized using UV-VIS technique and the results were systematically presented. Optical transmittance was affected for moderate doping.

Dispersion parameters of the films obeye the single oscillator model The change in dispersion was investigated before and after doping and its value increases from 19.52 for the un-doped films to 22.86 for the doped films with 7% of Ga. The optical conductivity of films was found to be increased as the doping concentration of Ga increases.

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