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Research paper

The study of transparent conducting gallium doped ZnO thin films in order to use in solar cells

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Abstract

In this study, transparent conducting Ga-doped ZnO thin films were deposited on glass substrate using chemical spray pyrolysis technique. The effect of Ga-doping concentration (0, 1, 2 and 3 at.%) on microstructural, optical and electrical characteristics of layers have been investigated. The studies of X-ray diffraction and optical transmission spectra show these films have a hexagonal wurtzite structure with (002) preferred growth direction, also a high transmission of 85-95% in visible range. Data analysis show that the band gap energies in these films are varying in the range of 3.27-3.33 eV, consistent with the Burstein-Moss shift effect, with Urbach tail widths between 114-160 meV. The 2 wt% Ga sample showed the maximum figure of merit (3×10-2Ω-1), with an electron concentration and sheet resistance of ~1.42×1019 cm-3 and 13 kΩ/square, respectively.

Keywords: *Thin Films; Spray Pyrolysis; Structural; Optical; Electrical; Ga Doped ZnO.*

1. Introduction

Optoelectronic devices like solar cells, light emitting diodes (LEDs) and liquid crystal displays (LCDs) require special type of materials called transparent conducting oxides (TCOs) [1]. Uniqueness of these materials is possession of both good electrical conductivity and visible light transmittance. Indium tin oxide (ITO) has been widely used as a TCO, but Zinc Oxide (ZnO) has gained a lot of research interest recently as a future TCO material because of the shortcomings of ITO which includes high cost, scarcity and toxicity . ZnO is an n-type II–VI semiconductor with large exciton energy of 60 meV and a direct wide band gap of 3.34 eV [2-4]. Zinc oxide has high chemical stability together with nontoxic in nature and high abundance, which makes it a lower cost material when compared to the most currently used transparent conducting oxides (ITO and SnO2). Several techniques such as sputtering [5], [6], thermal evaporation and spray pyrolysis have been applied for the production of ZnO. Spray pyrolysis is preferred due to its cheaper, simpler and more versatile than the others, which allows the property of obtaining films with the required properties for the different applications and also when large area of the films is needed. In this study, Ga-doped ZnO (hereafter GZO) thin films were prepared by Spray pyrolysis method since this particular technique offers several advantages, such as simple equipment, low fabrication cost, and high homogeneity of the precursor. We characterise the structural, electrical, and optical properties of GZO with various concentrations of 0, 1, 2 and 3 wt%. nanocrystaline thin films have been investigated and a number of optical and electrical parameters have been qualitatively calculated.

2. Experimental details

ZnO:Ga thin films were deposited on glass substrate using chemical spray pyrolysis technique by Spray Coating System (S.C.S–86) deposition set. The starting 0.2 M spray solution was made by Zinc acetate dehydrate (Zn $(CH_3COO)_2.2H_2O$, solved in a methanol and deionized water mixture (volume ratio of 3:1). A few drops of acetic acid were added to stabilize the starting solution. In order to study the influence Ga dopant concentrations on the properties of Ga-doped ZnO thin films, we used Gallium Nitrate ($GaN_3O_9.8H_2O$) in the starting material to obtain solutions with [Ga]/[Zn] wt% ratios of 1, 2 and 3 while all other parameters kept constant (i.e., precursor volume 50 ml, substrate temperature 450 °C, nitrogen flow rate 5 ml/min at a pressure of 2.5 bar while the distance between substrate and the nozzle is 33 cm). The crystalline structure of the films were obtained using the X-ray diffractometer with Cu-Kα radiation (Philips-pw- 1830), and optical properties studied with UV–VIS spectroscopy (Shimadzu–UV160) in the wavelength range of 350-1100 nm. To investigate the electrical properties of the films, including resistivity and Hall measurements, we used a four-probe van der Pauw configuration [9] with a magnetic field of 0.4 T.

3. Results and discussion

3.1. Structural studies of the films

The crystal structure, grain size and orientation of GZO thin films were investigated by X-ray diffraction (XRD) patterns. Fig. (1) shows the XRD spectrum of the studied samples. Several peaks were observed which corresponds to (002), (101), (103) planes that are all indexed to the hexagonal wurtzite structure of ZnO with space group P63mc(186) (JCPDS 36–1451) [19]. It is also observed that the films are polycrystalline in nature with (002) along the c-axis of the hexagonal structure as the preferred direction. Such preferred orientation is typically observed in Gallium-doped ZnO films [7], [8], [11].

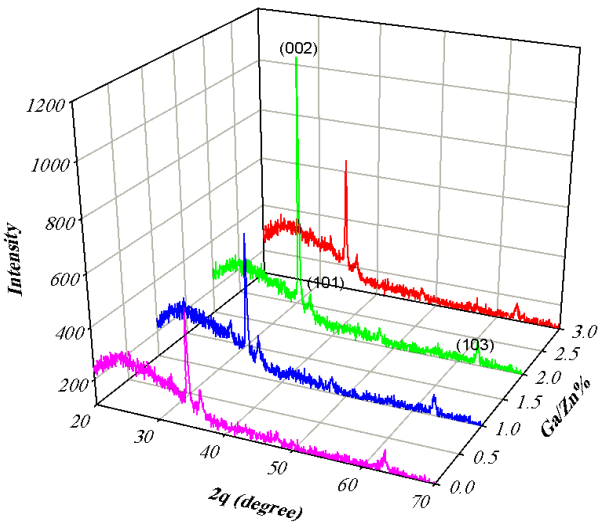

Fig. 1: Superimposed X-Ray Diagrams for the Zno: Ga Polycrystalline Thin Films Deposited with Different Impurity Concentrations.

The variations of average grain size (D) could be estimated from the XRD data using the Debye-Scherrer equation based on the (002) plane [9]:

$$D = \frac{0.9\lambda}{\beta\cos(\theta)} \quad (1)$$

Where λ is the x-ray wavelength (=1.54 Å), β is the line width of the half-maximum intensity (FWHM). The determined values in Table (1) show that average grain sizes are ranged from 26 to 32 nm.

Table 1: The Calculated Grain Size and Lattice Constants in GZO Samples

sample	2θ (drgree)	β	D(nm)
ZnO	34.643	0.312	26.660
1% GZO	34.639	0.311	26.743
2% GZO	34.597	0.272	30.578
3% GZO	34.585	0.263	31.165

These data are also used to calculate the lattice constants a and c from the (002) and (100) diffraction planes respectively using the following equation [10]:

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (2)$$

Where (h, k, l) are the Miller indices, a, c are the lattice constants and dhkl is the interplanar spacing. According to these calculations that are reported in Table 2, they are in good agreement with JCPD data cards, a=3.25, c=5.20 [5]. Moreover, sample containing 2 wt% Ga-doping has the highest (002) diffraction peak intensity. This indicates that increasing the doping concentration deteriorates the crystallinity of the films as a result of stress formation due to the difference in ionic sizes between zinc and the dopant and the segregation of dopants in grain boundaries [11].

Table 2: The Calculated Grain Size and Lattice Constants in GZO Samples

Sample	JCPDS	ZnO	1% GZO	2% GZO	3% GZO
a (nm)	3.249	3. 257	3.237	3.268	3.268
c (nm)	5.206	5.173	5.173	5.179	5.179

3.2. Optical studies of the GZO thin films

The knowledge of optical constants of materials is frequently of great interest in the design and analysis to be used in optoelectronics. It is possible to determine thickness and some important optical constants from transmission spectra . Fig. (2) shows the optical transmission spectra in the range 300–1100 nm. Obviously, all films exhibited an average transmittance higher than 80% in the range 400-81100 nm. As high transmission is desirable for solar cell application in order to use as transparent anti-reflecting electrode [12].

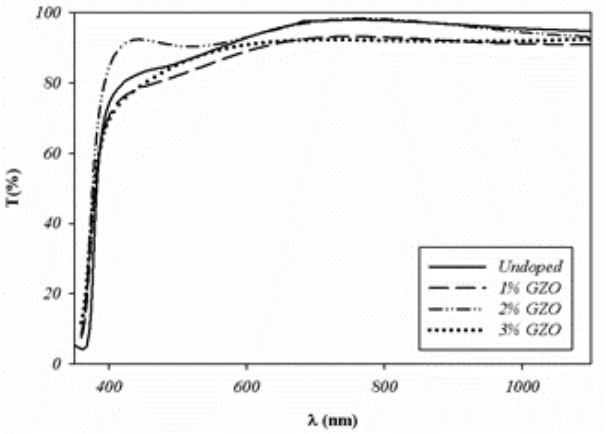

Fig. 2: Optical Transmittance Spectra of the Zno and GZO Thin Films.

The absorption coefficient was calculated from the optical transmition and Beer-Lambert relation [13]

$$\alpha = \frac{-1}{d} ln(T) \quad (3)$$

Where T(λ) is the transmittance wavelength dependent spectrum of the layer. The result of these calculations are shown in Fig. 3 as a diagram of α versuse wavelength.

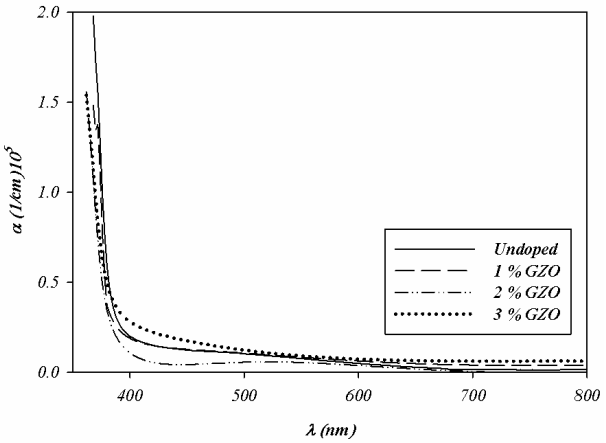

Fig. 3: Absorption Coefficients Spectra in Zno and Zno:Ga Samples.

It is evident that absorption coefficients in the ultraviolet region (λ < 400 nm) are larger than those in the visible region and decreases slowly with the increase of the Ga doping concentration. the absorption edge shifted to UV region when the concentration of Ga dopant increased from 0 to 2 wt%. It implies that increasing Ga doping concentration could decrease the optical absorption in the ultraviolet region.

The optical band gaps were estimated from the following relation [14]:

$$(\alpha h\nu) = A(h\nu - E_g)^m \quad (4)$$

Where A is an energy-independent constant, hν is the photon energy, B is a constant and Eg is the optical band gap. Optical band gap was determined by plotting the Tauc plot and extrapolating the linear part of the plot to the energy axes (Fig. 4). m is a constant, which determines the type of the optical transition. The values of the direct optical band gap Eg were obtained from the intercept of $(\alpha h\nu)^2$ versus hν curves, as shown in Fig. 4, with the inset as the magnified data close to the intercept region.

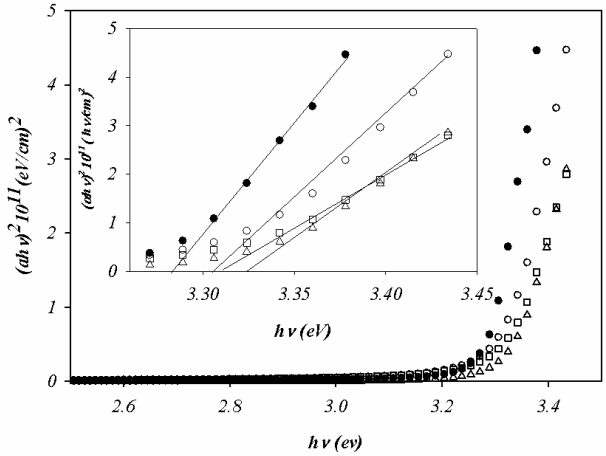

Fig. 4: Variation of $(Ahv)^2$ Versus (Hv) of the GZO Thin Films.

The band gap values were observed to increase from 3.27 to 3.33 eV as the Ga doping concentration increases from 0 to 2 wt% as shown in Table 2. The increase in optical band gap is in agriment with absorption edge shift to UV region and interpreted as the B-M effect where in heavily doped semiconductors like Ga doped ZnO the Fermi level lies within the conduction band meaning that electrons from the valence band will be excited to a position above the fermi level which lies within the conduction band owing to Pauli's exclusion principle [15]. On the other hand the decrease (red shift) of Eg for impurity concentrations above 2 wt%, could be due to either excess Ga atoms do not activate because of the segregation at the grain boundaries [11]. and/or increments of the localized states width mainly related to the impurities or oxygen vacancies close to the conduction band edge.

Table 2: The Calculated Band Gap and Band Tail Width in the GZO Samples

sample	ZnO	1% GZO	2% GZO	3% GZO
E_g (eV)	3.27	3.31	3.33	3.31
E_0 (meV)	119	158	114	159

To investigate the role of these intrinsic extrinsic defects we have studied the spectral dependence of the light absorption coefficient α at photon energies just below the energy gap of the films. The linear absorption coefficient below absorption edge follows the exponential law [16].

$$h\nu < E_g \quad \alpha(h\nu) = BE_0^{3/2} e^{h\nu/E_0} \tag{5}$$

Where E0 is the Urbach energy referred to the width of the localized states. The Urbach energy could be found using [17].

$$E_0 = \left[\frac{d\ln(\alpha)}{d(h\upsilon)}\right]^{-1} \tag{6}$$

The ln (α) vs. photon energy plot for the studied samples are shown in Fig. 5. The third raw in Table 3 represents E0 values. According to these results, compared with the undoped sample, in doped samples the E0 width is changed between ~4-00 meV. The increase depicts an increase in structural disorder [11].

3.3. Electrical properties of the GZO thin films

3.3.1. Resistivity and figure of merit

The electrical properties of the layer could affect on various optical parameters, such as reflection index, absorption coefficient, band gap, etc., of the films. Fig. 6 shows the measured sheet resistance (Rs) as a function of [Ga/Zn] ratio for the studied samples. From these data it is clear that in general: (1) compared to undoped sample by increasing the [Ga/Zn] ratio the corresponding sheet resistance of the layers decreases sharply (by a factor of ~100); (2) although sample with 2 wt% Ga doping has the minimum resistivity it gradually increases beyond this point. These statements could be explained in terms of the gradual replacement of Zn^{+2} ions into Ga^{+3} for ≤2 wt% doping. This process releases a free electron to the conduction band for every Ga ion incorporated into the lattice, and hence leads to an increase in the carrier concentration of the GZO thin films. However, the increase in the electrical resistance with further increase in doping concentration may be caused by disorder in ZnO lattice and/or segregation of dopants at the grain boundaries. It is known that an increase in the impurity concentration results in a decrease in the carrier mobility due to enhanced scattering. An increase in the charge carrier density beyond a certain limit can also result in reduced mobility of charge carriers and hence an increase in the resistivity [18].

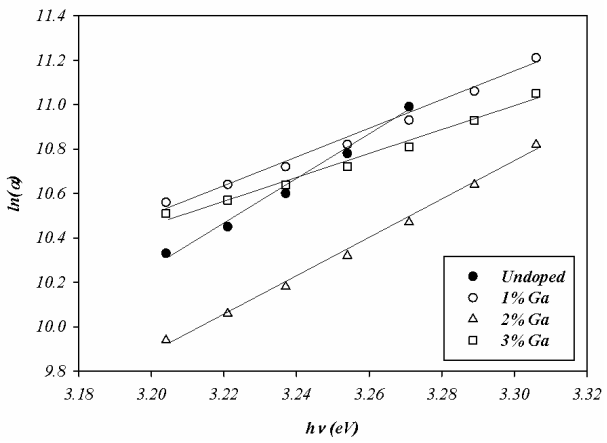

Fig. 5: The Variation of Logarithm of Absorption Coefficient versus Photon Energies Just Below the Absorption Edge, Eg, of the Films.

Figure of merit (ϕ) is a useful parameter in comparing transparent conductive thin films, especially those with the same material and under different deposition conditions. According to Haacke's definition [19]:

$$\varphi = \frac{T^{10}}{R_s} \tag{7}$$

Where T is the transmittance of film at 550 nm. Fig. 6 also shows the variations of the calculated figure of merit in these samples. As it is obvious sample with doping ratio of 2 wt% provides the maximum ϕ of 3×10^{-2} $(k\Omega)^{-1}$.

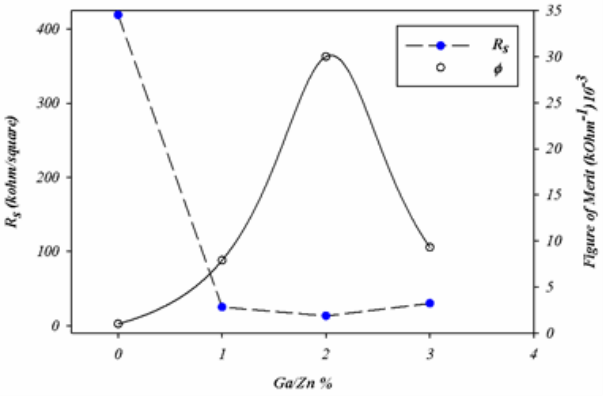

Fig. 6: The Measured Sheet Resistance and the Calculated Figure of Merit versus Ga Concentration in Various Samples.

3.3.2. Carrier concentration and mobility

We found that all the studied samples (pure and Ga-doped) show n-type conductivity. Although it is expected in pure stoichiometric ZnO we are faced with intrinsic behavior. It is found that due to the presence of oxygen vacancies and interstitial zinc atoms in undoped nonstoichiometric ZnO layers n-type conductivity occurs. Fig. 7

shows the measured carrier (electron) density (Ne), Hall mobility (μ) and resistivity (ρ=Rs/t) data against the impurity concentration in these samples at room temperature. As it is evident although the mobility of the carriers is not affected too much by doping concentration and varying ~ 4.5±2 cm^2/v.s, the electron density is considerably increased, about two orders of magnitude, from ~ 10^{17} cm^{-3} in undoped ZnO to ~10^{19} cm^{-3} in doped GZO samples. These variations are consistent with the role of Ga-atoms in the crystal, and the corresponding behavior in structural and optical properties of the films.

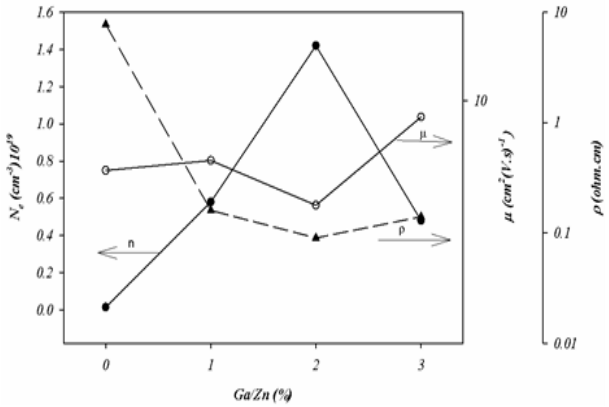

Fig. 7: Variations of Measured Sheet Resistance, Electron Density and Mobility at Room Temperature in Various Samples.

4. Conclusions

Structural, optical and electrical properties of undoped and Ga-doped (GZO) (0, 1, 2 and 3 wt%) thin (~150 nm) films grown by spray pyrolysis technique on glass substrate are studied. The XRD and transmittance spectra indicate that the films are of polycrystalline nature with hexagonal wurtzite crystal structure and preferred growth direction of (002) with high transmission of ~85-95% in the visible region. The physical properties were found to be sensitive to increasing Ga content. We found that the direct band gap and band tail width changes with Ga doped concentration. There was a blue shift in the absorption edge with increasing Ga which correlated well to the increasing optical band gap. Electrical measurements, including resistivity, carrier concentration and mobility, showed sample with 2 wt% Ga doping with the minimum resistivity of 0.09 Ω.cm has the highest figure of merit of 3×10^{-2} $(k\Omega)^{-1}$.

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