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Effect of annealing and In content on the properties of electron beam evaporated ZnO films

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Abstract. The effect of both annealing and In content on the properties of ZnO films prepared by electron beam evaporation were investigated. The evaporation was carried out at room temperature from bulk samples prepared by sintering technique. X-ray diffraction showed that the structure of ZnO-In_2O_3 films depends on both the In content and annealing temperature. Amorphous, highly transparent and relatively low resistive films which can be suitable for the usage as transparent electrode of organic light-emitting diode were obtained upon annealing at 300 °C. Partially crystalline, highly transparent and highly resistive films which can be used in piezoelectric applications were obtained upon annealing at 500 °C. For each composition the refractive index has no monotonic variation upon increasing annealing temperature.

PACS. 61.10.-i X-ray diffraction and scattering – 78.20.-e Optical properties of bulk materials and thin films – 68.55.-a Thin film structure and morphology – 72.20.-i Conductivity phenomena in semiconductors and insulators

1 Introduction

Transparent conducting (TCO) films are frequently used in numerous applications such as optoelectronic devices [1,2], surface acoustic wave devices [3], antistatic coatings, light-emitting, light-detecting, and light-triggered semiconductor devices, electrodes for electrochromic devices solar cells and smart windows [4–6]. Each application requires certain material properties. In many cases the desired properties could not be obtained using practical TCO films consisting of binary compounds. However new materials consisting of ternary compounds and/or multicomponent oxides are mainly used [7–9].

From all the TCO material studied, in the last years, zinc oxide (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties, high chemical and mechanical stability together with its abundance in nature, which makes it a lower cost material when compared with the most currently used TCO materials (ITO, SnO_2).

Amorphous transparent conductive ZnO films are currently important for the usage as a transparent electrode of organic light-emitting diode, because of their surface flatness and availability on plastic substrate. Etching characteristics are improved because the etching speed does not depend on the crystal orientation in the amorphous phase [10,11]. For film bulk acoustic device applications, it is necessary for ZnO films to be prepared with some specific characteristics. The first one is high resistivity [12], e.g. in an acoustic amplifier semiconductor a resistivity of 10^3 to 10^6 Ω cm is required [13].

The majority of investigations of ZnO has been concerned with films prepared by sputtering [3,7,10–12]. However published data on electron beam evaporation is relatively few. Therefore in this work we investigate the effect of In content and annealing on the structural, optical and electrical properties of electron beam evaporated ZnO films.

2 Experimental details

The appropriate ratios of ZnO (purity, 99.999%) and In_2O_3 inclusions (purity, 99.999%) powders were mixed and prepared in a tablet form using cold pressing technique. The sintering of the pressed powder mixture was carried out at 1000 °C for 4 h in air. The ratios of In/Zn in the tablets were 0, 1, 3, 5 and 7 at.%. Thin films of the considered ratios were prepared by electron beam evaporation in an Edward's high vacuum coating unit model 306 A under pressure of 5×10^{-6} and 8×10^{-5} torr before and during film deposition, respectively. The films were prepared on ultrasonically cleaned corning glass substrates held at room temperature. The thickness of the films (≈100 nm) was controlled using digital film thickness monitor model TM 200 Maxtek. The

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deposition rate was ≈0.5 nm/s. The as-prepared films were annealed in air for 1 h. The full set of annealing temperatures was 100, 200, 250, 300, 400 and 500 °C.

The crystallinity of the as-prepared and heat treated films were examined using a Diano Corporation X-ray diffractometer. CoK_α radiation ($\lambda = 1.79026$ Å) was used from the X-ray tube with normal focus. The optical transmittance (T) and reflectivity (R) of the as-prepared and heat treated ZnO-In_2O_3 films were studied using Jasco 570 double beam spectrophotometer in a wave length (λ) 200–2500 nm range at normal incidence. The resistivity measurements were carried out using two-terminal configuration by applying constant voltage (≈5 V) to the sample and measuring the current through it using Keithley 614 electrometer. The measurements were achieved at room temperature. Electrical contacts were made by applying silver paste over the surface of the films with separation of 2 mm.

3 Results and discussion

3.1 Structural examination

Figure 1a–e shows XRD patterns of as-prepared ZnO-In_2O_3 films. The absence of diffraction peaks from Figure 1a–b indicates that as-prepared undoped ZnO films and the films prepared with 1 at.% In have amorphous structure. This amorphous nature may be due to the large number of defect sites arising from oxygen atom vacancies [14]. The addition of 3 at.% In leads to crystalline peaks. The amount and intensity of these crystalline peaks increase with increasing In content to 7 at.%. From the JCDPS files the diffraction peaks can be identified as Zn and In elements (JCDPS card No. 04-0831 and 05-0642, respectively). The appearance of Zn and In diffraction peaks refer to a very big reduction to the evaporated ZnO-In_2O_3 oxides and to a larger number of oxygen atom vacancies. Upon annealing at 250 °C the films oxidised, the Zn and In diffraction peaks disappeared and amorphous structure are obtained (figure is not shown). At 300 °C small crystalline peaks characterizing ZnO (JCDPS card No. 36-1451) are observed for pure ZnO films and films prepared with 1 at.% In (Fig. 2a–e), and no indication for In_2O_3 peaks. At 500 °C the intensity of ZnO increased slightly (Fig. 3a–e). It is noticed that the doped films with a doping level higher than 1 at.% still amorphous even after annealing at 500 °C (Fig. 3c–e). This indicates that the higher In content stabilizes the amorphous structure for ZnO films.

Tominaga et al. [10] have reported that ZnO crystallizes at room temperature, so the preparation of amorphous ZnO is very difficult. Therefore, they used a DC facing target planer magnetron sputtering apparatus to prepared amorphous ZnO-In_2O_3 films from ZnO and In_2O_3 targets. The substrate temperature was 150 °C and the current ratio $\delta = I_{Zn}/(I_{Zn} + I_{In})$ was selected as the parameter for deposition. All the obtained films were oxygen rich. At $\delta < 0.11$ polycrystalline In_2O_3 films were obtained, while amorphous films were obtained in the region

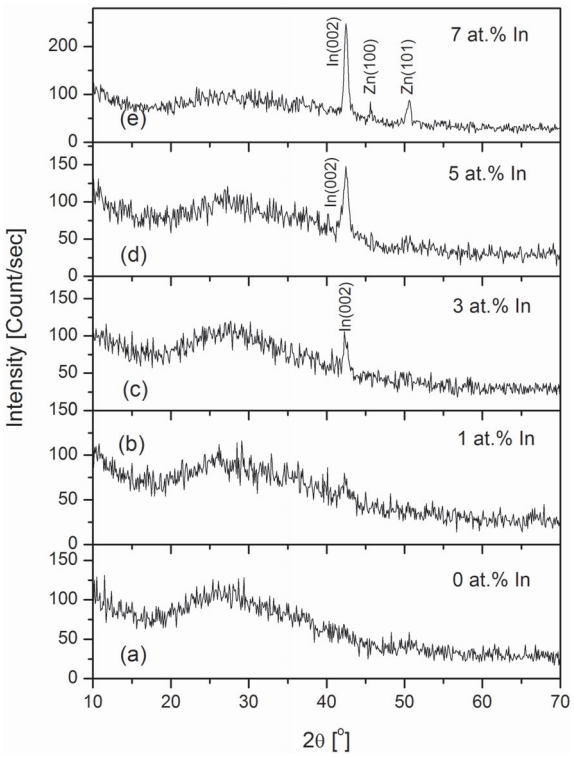

Fig. 1. X-ray diffraction patterns of as-prepared ZnO-In_2O_3 thin films.

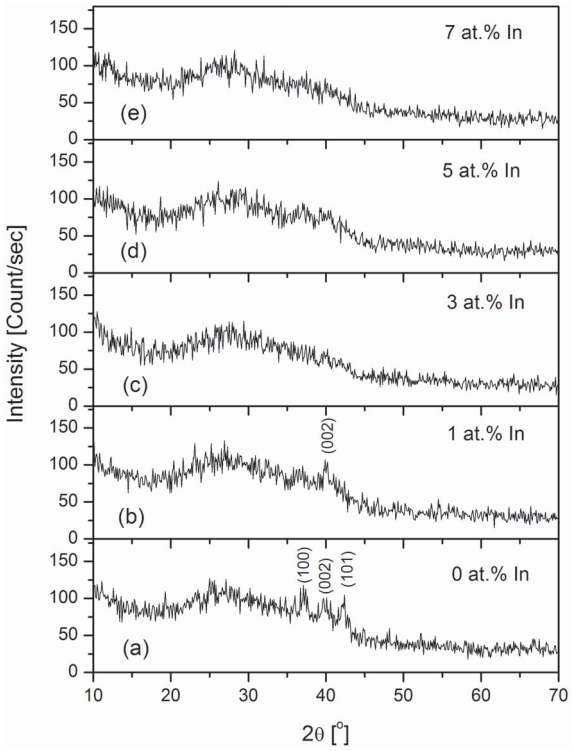

Fig. 2. X-ray diffraction patterns of ZnO-In_2O_3 thin films annealed at 300 °C.

$0.20 < \delta < 0.67$. The phases obtained at $\delta = 0.73$ and 0.80 were assigned to homologous $Zn_3In_2O_6$ and $Zn_{11}In_2O_{14}$,

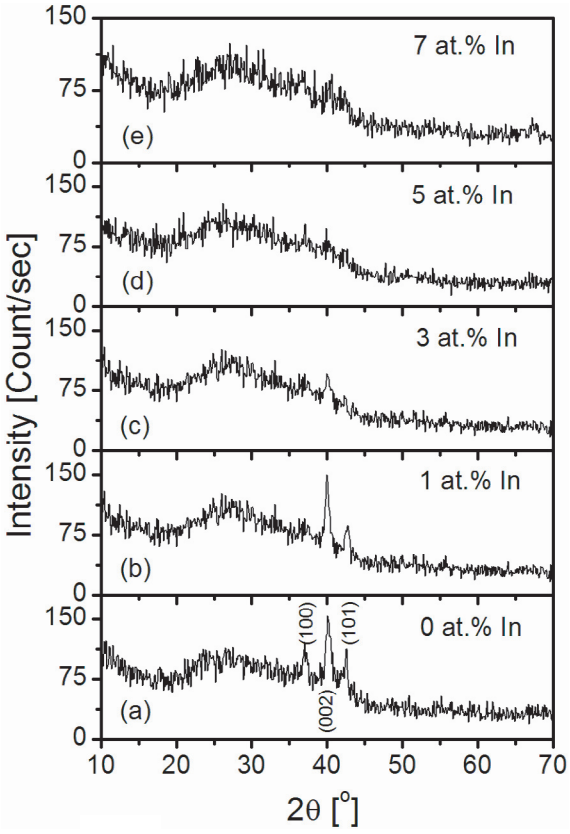

Fig. 3. X-ray diffraction patterns of ZnO-In_2O_3 thin films annealed at 500 °C.

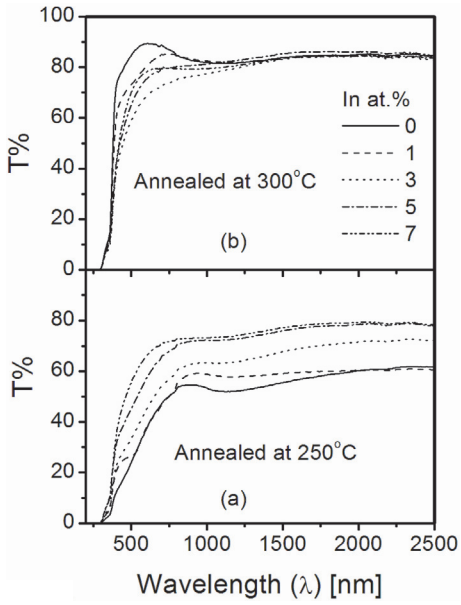

Fig. 4. Transmittance spectra of ZnO-In_2O_3 thin films annealed in air for 1 h at (a) 250 °C and (b) 300 °C.

respectively. Recently, the same group [11] has studied the influence of the Al_2O_3 impurities on the properties of In_2O_3-ZnO films. They found that the threshold δ value at which In_2O_3-ZnO films change from amorphous to homologous phase is nearly constant at $\delta = 0.67$ for $Al_2O_3 = 0, 2$ and 3 wt.%. Moriga et al. [15,16] have found that: (i) with the increase of the substrate temperature to 300 °C the amorphous structure of the films obtained in the region $0.20 < \delta < 0.67$ disappeared and crystalline phases were obtained [15]; and (ii) the compositional range where amorphous films formed was widened by the introduction of argon during the preparation of ZnO-In_2O_3 films by pulsed laser deposition [16]. In our case and by using our preparation method, at higher In content ZnO films remain amorphous even at the highest (500 °C) annealing temperatures. Thus, by controlling In content and annealing temperature, amorphous ZnO can be easily obtained.

3.2 Optical properties

As described in the experimental section, the optical transmittance and reflection were measured in the wave length range 200–2500 nm. The average transmittance of the as-prepared ZnO-In_2O_3 films is lower than 25%. After annealing, in air for 1 h, the transmittance improved gradually due to the oxidation. Figure 4a–b shows the transmittance of the films annealed at 250 and 300 °C, respectively. It is seen from Figure 4a that the pure ZnO has lower transmittance and both the shift of the onset transmittance and the average transmittance increase with increasing the In content. On the contrary, the shift of the onset transmittance for the films annealed at 300 °C remains approximately constant with increasing In content. The poor transmittance in Figure 4a is ascribed to the probable metal inclusions of these 250 °C annealed films. The annealing at temperatures higher than 300 °C leads to small change in transmittance.

The optical bandgap (E_g) can be quantitatively derived by applying a relation of the type

$$(\alpha h\nu) = \beta\,(h\nu - E_g)^{\eta} \tag{1}$$

in the spectral range where the absorption is strong. In equation (1) β is a constant, ν is the frequency, h is Plank's constant and α is the absorption coefficient. The exponent η depends on the kind of optical transitions that prevail, and thermal broadening is neglected. For crystalline semiconductors, η is 1/2, 3/2, 2 and 3 when the transitions are direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively. In the case of an amorphous semiconductor η should be 2 as a result of the non-conservation of the wavevectors; under the last conditions one speaks of "Tauc gap" [17,18]. There are some notable exceptions to the quadratic frequency dependence of the absorption coefficient, and it should not therefore be regarded as a characteristic phenomenon of amorphous semiconductors. The absorption coefficient in amorphous Se [17] and partially amorphous $Bi_{1.5}Sb_{0.5}Se_3$ composition [18] exhibits a relation in the form

$$(\alpha h\nu) = \beta\,(h\nu - E_g)\,. \tag{2}$$

Certain multicomponent materials [17] have been found to have an absorption coefficient that obeys the relation

$$(\alpha h\nu) = \beta\,(h\nu - E_g)^3\,. \tag{3}$$

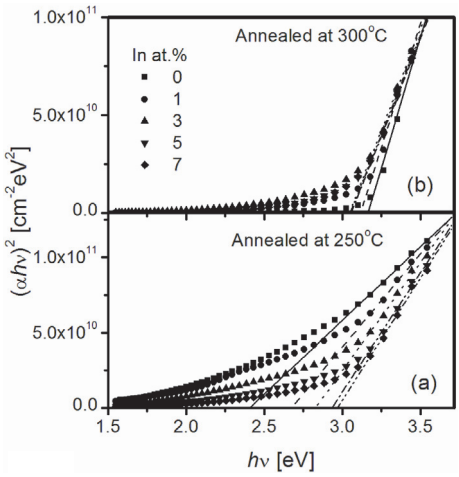

Fig. 5. Optical band gap determined by extrapolation of the straight section of $(\alpha h\nu)^2$ versus photon energy for ZnO-In_2O_3 films; (a) annealed at 250 °C and (b) annealed at 300 °C.

In our case, the optical absorption coefficient was found to obey a relation of the kind

$$(\alpha h\nu) = \beta\,(h\nu - E_g)^{1/2} \tag{4}$$

which indicates a direct transition. Therefore the E_g values were determined by extrapolation of the straight section of the square of the $\alpha h\nu$ versus photon energy ($h\nu$), as illustrated in Figure 5a, b for ZnO-In_2O_3 films annealed at 250 and 300 °C, respectively. The optical band gap values determined at different temperatures are listed in Table 1. It is seen from Table 1 that E_g increases with increasing annealing temperature. This increase in E_g can be ascribed to: (i) the reduction in defect centers (oxygen vacancies) as the stoichiometry improved upon oxidation; and (ii) the structure transformation from multiphase system to be close to single phase ZnO. The last reason comes from the fact that our films did not obey the quadratic frequency dependence of the absorption coefficient proposed for amorphous semiconductors. The E_g values for films annealed at 250 °C increases with increasing In content while it remains approximately constant with increasing In content for films annealed at temperatures higher than 250 °C. The last observation is consistent with Naghavi et al. [20], for In_2O_3-ZnO films prepared by pulsed laser deposition, where they found that at higher zinc content (Zn/(Zn + In) > 0.80) E_g values remains constant at 3.4 eV. The E_g values determined upon annealing at the temperature range 300–500 °C are comparable with ZnO-In_2O_3 values 3.15–3.32 eV obtained by El Rhaleb et al. [9] using spray pyrolysis technique.

The values of the refractive index (n) were calculated using the following relation [21,22]

$$n = \frac{1+R}{1-R} + \left[\left(\frac{R+1}{R-1}\right)^2 - \left(1+k^2\right)\right]^{1/2} \tag{5}$$

where $k = \alpha\lambda/4\pi$ is the extinction coefficient. Figure 6 shows the variation of refractive index (n at 550 nm), determined from films annealed at different temperatures, as a function of In content. At each annealing temperature the refractive index increases with increasing In content up to 3 at.%, then it decreases again. On the other hand, for each composition the refractive index has no monotonic character with increasing annealing temperature. Our refractive index values are slightly lower than the values (2.1 to 2.4 in the visible range) obtained by Minami et al. [7] for ZnO-In_2O_3 films prepared at 350 °C by magnetron sputtering deposition.

Table 1. Optical band gap values of ZnO-In_2O_3 thin films determined at different annealing temperatures.

In content (at.%)	E_g 250 °C	300 °C	400 °C	500 °C
0	2.41	3.16	3.18	3.17
1	2.67	3.12	3.16	3.17
3	2.83	3.04	3.07	3.09
5	2.93	3.05	3.06	3.08
7	2.97	3.05	3.09	3.09

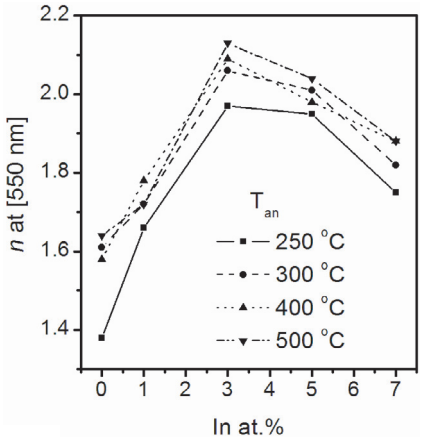

Fig. 6. Variation of refractive index (at 550 nm) as a function of In content.

3.3 Electrical resistivity

The electrical resistivities of ZnO-In_2O_3 films are listed in Table 2. It is seen that the as-prepared ZnO films has a resistivity of $1.2\times10^{-2}\ \Omega\,\mathrm{cm}$. This value increases with increasing In content to $1.6\times10^{-1}\ \Omega\,\mathrm{cm}$ at 5 at.%. The electrical resistivity values increase slowly with annealing up to 300 °C. At 400 °C a much steeper increase is observed. At 500 °C the resistivity has a little decrease. The higher resistivity values obtained for films annealed at temperatures 300, 400 and 500 °C can be ascribed, as Mitsuyu et al. [3] reported, to oxygen reactions with ZnO. For example, absorbed oxygen removes zinc interstitials (Zn_i) and/or oxygen vacancies (V_o), thus reduces the density of these donor-like defects and carrier density. The Zn_i and V_o can be reduced thermally by the variation of

Table 2. Room temperature resistivity values of ZnO-In_2O_3 thin films determined at different annealing temperatures.

In content (at.%)	25 °C	100 °C	200 °C	250 °C	300 °C	400 °C	500 °C
0	1.3×10^{-2}	2.4×10^{-2}	1.9×10^{-2}	1.6×10^{-2}	9.1×10^{-1}	4.4×10^{6}	3.8×10^{6}
1	1.4×10^{-2}	1.8×10^{-2}	1.0×10^{-2}	7.8×10^{-2}	4.3×10^{-1}	4.4×10^{6}	3.5×10^{6}
3	7.1×10^{-2}	8.1×10^{-2}	1.1×10^{-1}	2.2×10^{-1}	9.9	4.3×10^{6}	3.9×10^{6}
5	1.6×10^{-1}	2.0×10^{-1}	3.0×10^{-1}	8.0×10^{-1}	4.4×10^{-1}	4.5×10^{6}	4.1×10^{6}
7	3.0×10^{-2}	9.2×10^{-2}	9.7×10^{-2}	6.4×10^{-1}	1.0×10^{-1}	3.4×10^{6}	3.0×10^{6}

oxygen pressure and temperature, according to equations (6) or (7) [23]

$$\mathrm{Zn}_i + 1/2\mathrm{O}_2\ (\mathrm{gas}) \rightarrow \mathrm{ZnO}\ (\mathrm{lattice}) \quad (6)$$

$$\mathrm{Zn}_i\ (\mathrm{lattice}) + V_o + 1/2\mathrm{O}_2\ (\mathrm{gas}) \rightarrow \mathrm{ZnO}\ (\mathrm{lattice}). \quad (7)$$

The big increase in resistivity was reported by other authors. Zhang and Brodie [24] reported that annealing of pure ZnO film, prepared by ion-beam assisted deposition, in air could raise resistivity about nine orders (10^{-3}–10^{6} Ω cm). Mitsuyu et al. [3] reported that the resistivity of rf-sputtered single crystal ZnO films increased about two-three order (10^{3}–10^{6} Ω cm). Chu et al. [12] found that postdeposition annealing of ZnO could make the ZnO films with higher resistivity, stronger c-axis (002) orientation, denser structure and relieved stress (i.e. the quality of ZnO films improved), even in a vacuum circumstances. The little decrease observed in the resistivities of the films annealed at 500 °C may be due to the oxygen out-diffusion from ZnO [25].

4 Conclusion and summary

ZnO-In_2O_3 films were prepared using electron beam evaporation from bulk samples prepared by sintering technique. The evaporated pure and mixed oxides were reduced and opaque films were obtained. Using an appropriate annealing temperature amorphous or partially crystalline ZnO films could be obtained. The increase of In content could inhibit ZnO crystallization. Upon annealing at temperatures from 200 to 300 °C the transmittance were found to increase, while annealing at 400 then 500 °C the transmittance changed slightly. At annealing temperature of 250 °C, the E_g was found to vary with In content, while at annealing temperatures higher than 250 °C the E_g values remain approximately constant. Highly transparent and low resistive films were obtained upon annealing at 300 °C. The annealing at 400 °C could raise the room temperature resistivity about seven orders of magnitude.

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