Influence of the doping with third group oxides on the properties of zinc oxide thin films

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The study of modifications in structural, optical and electrical properties of vacuum evaporated zinc oxide thin films on doping with III group oxides namely aluminum oxide, gallium oxide and indium oxide are reported. It was observed that all the films have transmittance ranging from 85 to 95%. The variation in optical properties with dopants is discussed. On doping the film with III group oxides, the conductivity of the films showed an excellent improvement of the order of $10^3\,\Omega^{-1}\mathrm{cm}^{-1}$. The measurements of activation energy showed that all three oxide doped films have 2 donor levels below the conduction band.

1. Introduction

Among the different II–VI semiconductor thin films, zinc oxide thin films are technologically important due to their range of electrical and optical properties. The excellent combination of electrical conductivity and optical transparency of these films make them well suited for the applications such as thin film transistors [1], thin film solar cells [2] and transparent electrodes [3].

Different deposition techniques such as R.F sputtering [4], pulsed laser deposition [5], spray pyrolysis technique [6] and sol-gel method [7] have been employed to obtain good quality of ZnO thin films. However, recently a greater interest has been focused towards the doping of ZnO thin film and improving its conductivity. Since zinc oxide is an *n*-type semiconductor, *n*-type doping is much easier compared to *p*-type doping. Doping with aluminum (Al), gallium (Ga) and indium (In) has been attempted by many research groups using different deposition techniques and with different source of dopants, resulting in high quality ZnO thin films [8–11].

Despite of the interest in ZnO thin films not much attention has been given towards its preparation by vacuum evaporation method. This method is relatively simple and low cost procedure. It does not require any catalyst or high temperature growth and the temperature of further oxidation of the film is moderate enough to be easily applied in thin film technology. The oxidation mechanism and the effect of annealing of vacuum evaporated ZnO thin films have been already reported [12–14]. In addition, least interest has been paid towards the doping of vacuum evaporated ZnO thin films.

The present work concentrated on the study of structural, optical and electrical properties of vacuum evaporated ZnO thin films and evaluation of property variation of these films on doping with aluminum oxide (Al_2O_3), gallium oxide (Ga_2O_3) and indium oxide (In_2O_3) separately. In this work, an attempt is made to obtain highly conducting transparent and oxide doped ZnO thin films through vacuum evaporation technique.

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2. Experimental procedure

Zinc oxide thin films obtained in this study were prepared by thermally evaporating high quality ZnO powder (Alfa Aesar 99.99%) using tungsten boats. Glass slides maintained at room temperature were used as substrates. The vacuum maintained prior and during the deposition was in the order of 10^{-5} Torr. For the preparation of doped films a mixture of 95% of ZnO powder and 5% dopant powder is evaporated maintaining other deposition parameters same as that of undoped films. The three different dopants used in this study are Al_2O_3, Ga_2O_3 and In_2O_3, each of purity 99.9% (Alfa Aesar). The thickness of the film is found by gravimetric analysis and it is observed to be 200 nm for all the films used in further characterizations.

During the process of evaporation, ZnO powder decomposes in to zinc and atomic oxygen according to the evaporation kinetics of ZnO and oxygen will be released as the primary by-product of the process [15]. Thus, films obtained are expected to be oxygen deficient in the as deposited condition and films are found to be dark brown in colour and opaque in nature. Hence, all doped films were annealed at 300°C for 2 h for further oxidation [12]. During the process of annealing films will undergo oxidation and there will be an improvement in the stoichiometry of the films. All films turn transparent after annealing. Similar observations are reported in the case of improvement in stoichiometry of thermally evaporated ZnO thin films after annealing [12–14]. After annealing, the films were further subjected to detailed structural optical and electrical characterization. Structural characterization of the obtained ZnO thin films was studied by X-ray JEOL diffractometer. The Scanning Electron Microscopy (SEM) studies to analyze the surface morphology of the films were performed with JEOL JSM 6380 system. Corresponding results are listed Fig 1–4. Transmittance and absorbance measurements were carried out relative to the uncovered substrate at normal incidence in a spectral range of 250–850 nm using Ocean Optics Inc SD 2000 UV-VIS spectrometer. Results are given in Fig. 5. The electrical characterizations of the ZnO thin films carried out on films of coplanar structures consisting of 2 silver

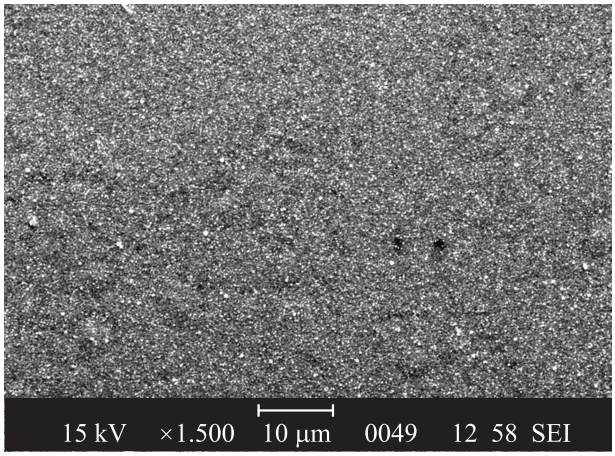

Figure 1. SEM image showing the surface topography of undoped ZnO thin film.

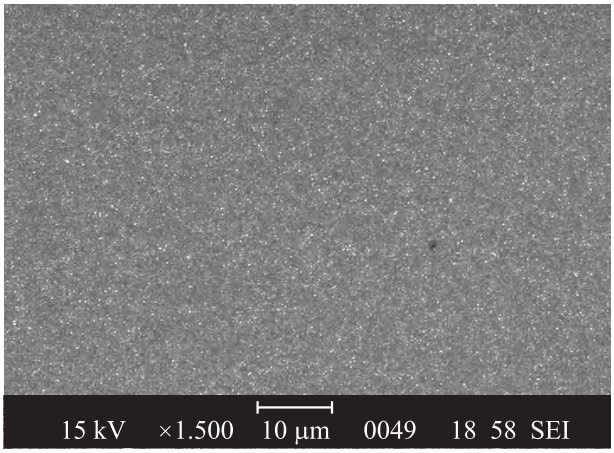

Figure 3. SEM image showing the surface topography of $ZnO:Ga_2O_3$ thin film.

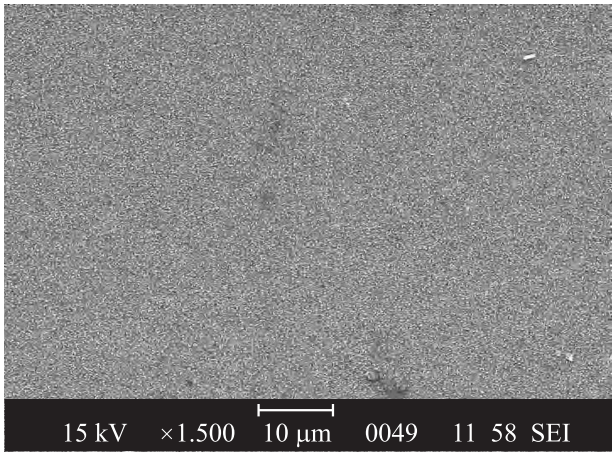

Figure 2. SEM image showung the surface topography of $ZnO:Al_2O_3$ thin film.

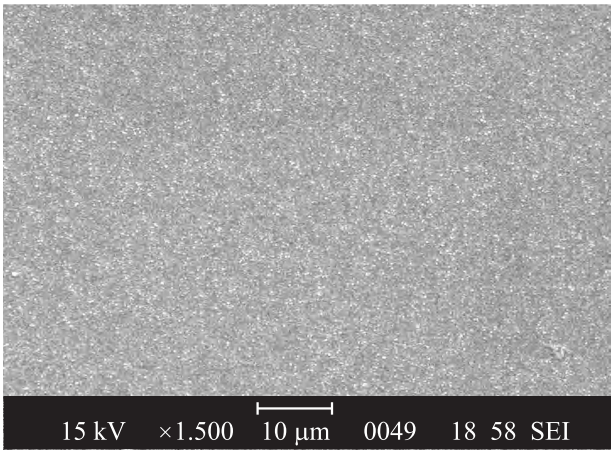

Figure 4. SEM image showing the surface topography of $ZnO:In_2O_3$ thin film.

strips evaporated on the film surface (Fig. 6). Computer assisted Keithley source meter (2400) setup was used for the electrical measurements in this work.

3. Results and discussions

X-ray diffractograms of undoped ZnO films, as well as 3 oxide doped ZnO films which include, aluminum oxide doped ZnO films ($ZnO:Al_2O_3$), gallium oxide doped ZnO films ($ZnO:Ga_2O_3$) and indium oxide doped ZnO films ($ZnO:In_2O_3$), did not show any peak in the θ range of 20 to 80°. This confirms the amorphous nature of the films.

The scanning electron micrographs of the surface of the undoped ZnO, $ZnO:Al_2O_3$, $ZnO:Ga_2O_3$ and $ZnO:In_2O_3$ films are shown (Fig. 1–4). By analyzing the micrographs, it is found that all films have smooth, continuous and pinhole free microstructure and hence it is clear that the surface topography of the films did not modify with dopants. This amorphous nature with flat and smooth surface of films will lead to the low internal stress and are well suited for the application of flat panel displays [16].

Fig. 5 shows the transmittance spectra of undoped as well as oxides doped ZnO films. Undoped ZnO films are found to have transmittance of above 90% in the visible region of the electromagnetic spectrum. On doping the film with In_2O_3, the average transmittance of the film remained almost same as that of undoped film whereas the transmittance decreased up to 85% on doping with Ga_2O_3. Interestingly in the case of $ZnO:Al_2O_3$ films the transmittance is better than the pure ZnO film and it is found to be above 95%. Jimenez et al [17] and Aladdine et al [18] made the similar observation. Thus, it can be concluded from spectra analysis that the doping of Al_2O_3 in ZnO thin film leads to a significant improvement in the transmittance of the film.

The optical energy gap „E_g“, of undoped and doped films is estimated from optical measurements. Since ZnO is a direct band gap semiconductor, the allowed direct transitions

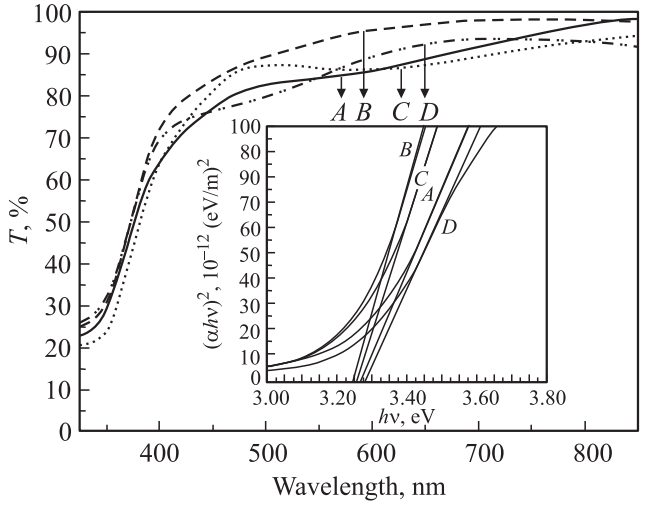

Figure 5. Transmittance spectra and optical band gap of undoped ZnO (*A*), $ZnO:Al_2O_3$ (*B*), $ZbO:Ga_2O_3$ (*C*) and $ZnO:In_2O_3$ (*D*) thin films.

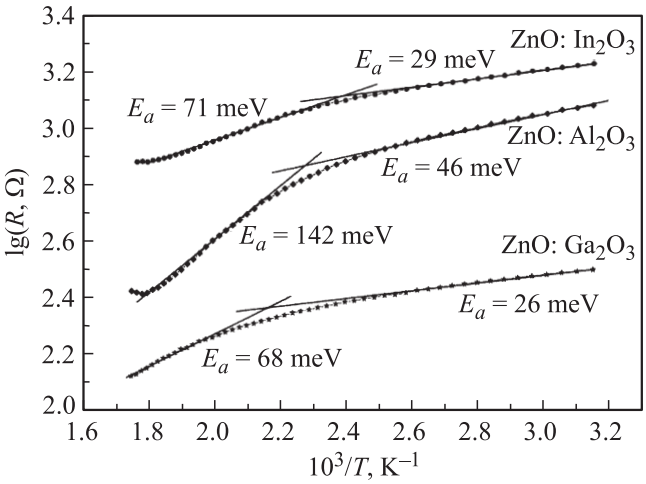

Figure 6. Logarithmic resistance profile with respect to reciprocal of temperature for $ZnO:Al_2O_3$, $ZnO:Ga_2O_3$ and $ZnO:In_2O_3$ thin films.

in the film can be assumed and the spectral dependence of the absorption coefficient, α can be described using the equation (1) [19].

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

where B is a constant.

The variation of $(\alpha h\nu)^2$ with $h\nu$ (photon energy) is plotted and the linear portion of the plot is extrapolated to zero to find the band gap of the film (Inset of Fig. 5). It is calculated and observed that the band gap of the undoped film is 3.27 eV. In the cases of doping, $ZnO:Al_2O_3$ film is having a band gap of 3.25 eV, and $ZnO:Ga_2O_3$ film is having a band gap of 3.26 eV. On doping the film with In_2O_3, band gap widening is observed and is found to be 3.28 eV. The reduction in the band gap in the cases of $ZnO:Al_2O_3$ and $ZnO:Ga_2O_3$ films may be due to the formation of additional levels below the conduction band in the electronic structures. Whereas the widening of the band gap in the case of $ZnO:In_2O_3$ film is generally attributed to the Burstein–Moss shift [20], which results from the filling of electronic states near the bottom of conduction bands, due to the increase of carrier concentration in the ZnO film. In this process apparent band gap of a semiconductor is increased as the absorption edge is pushed to higher energies, because of all states close to the conduction band being populated. Tokomoto et al. also made the same observation when the ZnO thin film grown by spray pyrolysis method is doped with indium [21].

The room temperature conductivity of the undoped film is found to be $90\,\Omega^{-1}\cdot cm^{-1}$. This conductivity is considerably high as compared to previously reported results on the conductivity of undoped ZnO thin films [5,22,23].

On doping the films with third group oxides, an excellent improvement in the room temperature conductivity of the order of $10^3\,\Omega^{-1}\cdot cm^{-1}$ is observed. The room temperature conductivity of the $ZnO:In_2O_3$ film is found to be $3.8\cdot 10^3\,\Omega^{-1}cm^{-1}$, for $ZnO:Al_2O_3$ film the conductivity is found to be $5.0\cdot 10^3\,\Omega^{-1}cm^{-1}$, and in the case of $ZnO:Ga_2O_3$ film the conductivity is better compared to other two films and is found to be $8.7\cdot 10^3\,\Omega^{-1}cm^{-1}$.

This high conductivity obtained due to the doping of III group oxides can be explained by considering the equation (2) [24].

$$M_2O_3 \rightarrow 2M + 2e' + \frac{1}{2}O_2 \qquad (2)$$

where notation M stands for metal.

According to equation (2) it is assumed that on adding III group oxides like Al_2O_3, Ga_2O_3 and In_2O_3 to ZnO, III group dopant atoms (Al, Ga and In) will get released. Since these atoms have one valance electron more than zinc they act as donors. The additional electrons, which are released in this process to equation (2) and not required for the bonding, are transferred to the conduction band. These additional electrons also contribute in improving the conductivity of the film. Thus, on doping with third group oxides a very good improvement in the conductivity of ZnO film is observed. Since the film in this case are amorphous, the absence of grain boundaries excludes the associated carrier scattering mechanism and thus higher performance of the material is expected [25].

To calculate the activation energy of doped films the variation in the resistance of the films with the change in temperature is recorded. The study was carried out by increasing the temperature of the films up to 300°C from room temperature. In this low temperature, extrinsic conduction predominates since ZnO film has a wide band gap above 3.3 eV. The semiconducting nature of the films

Opto-electronic properties of undoped and III group oxide doped ZnO thin films

Sample nature	Optical band gap (eV)	Transmittance T(%)	Room temperature conductivity (Ω^{-1}cm^{-1})	Shallow donor level (meV)	Deep donor level (meV)
Undoped ZnO film	3.27	90	90	–	–
$ZnO:Al_2O_3$ film	3.25	95	$5.0 \cdot 10^3$	43	142
$ZnO:Ga_2O_3$ film	3.26	85	$8.7 \cdot 10^3$	26	68
$ZnO:In_2O_3$ film	3.28	90	$3.8 \cdot 10^3$	29	71

follows the relation given in (3) [26].

$$R = R_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (3)$$

where R is the resistance of the film at temperature T, R_0 is a constant, k_B is Boltzmann constant and E_a is the activation energy required for conduction.

A representative graph of variation of $\lg R$ with the reciprocal of temperature $(1/T)$ for all the three oxide doped films is shown Fig. 6. From the logarithmic resistance profule with respect to reciprocal of temperature, the thermal activation energy is calculated using the equation (4).

$$E_a = [2.303 k_B (\text{slope})]/e \quad (4)$$

where e — magnitude of charge on electron.

In the graph (Fig. 6) $\lg R$ verses $1000/T$, for all oxide doped films, curve shows a linear behaviour in two regions. On these two ranges the activation energy is proportional to the slope. $ZnO:Ga_2O_3$ film presents activation energy of 26 meV in the $1000(1/T)$ range (2.3–3.2 [1/K]) and activation energy of 68 meV in the $1000(1/T)$ range (1.7–2 [1/K]). For the case of $ZnO:Al_2O_3$ film we determine an activation energy of 43 meV in the $1000(1/T)$ range (2.3–3.22 [1/K]) and activation energy of 142 meV in the $1000(1/T)$ range (1.7–2 [1/K]) and in this case an inflection point is observed above $1000\,1/T = 1.5\,\text{K}^{-1}$. Finally in the case of $ZnO:In_2O_3$ an activation energy of 29 meV was measured in the $1000(1/T)$ range (2.3–3.22 [1/K]) and another of 71 meV in $1000(1/T)$ range (1.7–2) [1/K]. Basically electron concentration in ZnO thin film increases by III group oxide doping and the trapping levels with activation energy bellow 55 meV contribute to the electrical conductivity with very low energy cost which improves the dark conductivity of the film [17].

The opto-electrical properties of undoped and oxide doped ZnO films studied in this work are furnished in Table.

4. Conclucions

In this paper we have shown the possibility of growing oxide doped ZnO films, possessing good optical, electrical and structural properties by the thermal evaporation technique. The modulation of the properties of the film on doping with third group oxides namely Ga_2O_3, In_2O_3 and Al_2O_3 is studied. All the films are shown to have transparency varying from 85–95% in the visible region and it is confirmed that doping of Al_2O_3 to ZnO film leads to the improvement in the transparency of the film. An excellent conductivity in the order of $10^3\,\Omega^{-1}\text{cm}^{-1}$ is achieved on doping the ZnO film with III group oxides. Through the measurements of activation energy it is shown that $ZnO:Al_2O_3$, $ZnO:Ga_2O_3$ and $ZnO:In_2O_3$ films have shallow donor levels at 46, 26 and 29 meV respectively. A deeper donor level is located at 142, 68 and 71 meV for $ZnO:Al_2O_3$, $ZnO:Ga_2O_3$ and $ZnO:In_2O_3$ films respectively, which are not ionized at room temperature. The structural characterizations of undoped as well as oxide doped ZnO films prove the amorphous nature and smooth surface topography of films without significant modification with dopant addition. Thus, III group oxide doped ZnO films with an excellent combination of transparency, conductivity and with smooth surface topography, well suited for the application of transparent electrodes in flat panel displays, can be obtained by thermal evaporation technique.

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