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Highly conducting and transparent Ga_2O_3 doped ZnO thin films prepared by thermal evaporation method

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Amorphous zinc oxide thin films are obtained by thermally evaporating pure zinc oxide powder. Films obtained have an excellent conductivity of $90\,\Omega^{-1}\,\text{cm}^{-1}$ with transparency of up to 90% in the visible region. On doping with gallium oxide a great improvement in the conductivity of up to $8.7 \cdot 10^3\,\Omega^{-1}\text{cm}^{-1}$ is observed and the optical band gap of the films is decreased from 3.25 to 3.2 eV, retaining the transparency. Measurements of activation energy show that the doped ZnO film has one donor level at 68 meV and other at 26 meV bellow the conduction band.

1. Introduction

With recent demand for large and high quality flat panel displays, amorphous transparent conducting films have attracted significant attention because of their flat and smooth surface and low internal stress [1]. Among the different materials which belong to the category of transparent conducting oxides, zinc oxide, which is one of the II-VI semiconductors, is a promising material due to its low cost, relatively low deposition temperature, good stability in hydrogen plasma compared with ITO and SnO_2 and non toxicity [2,3]. Good quality of ZnO thin films can be obtained by different deposition techniques such as, r.f sputtering [4], pulsed laser deposition [5], spray pyrolysis technique [6] and sol-gel method [7]. Recently research groups are much interested in the doping of ZnO thin film and improving its conductivity. Since zinc oxide is basically *n*-type semiconductor, *n*-type doping is much easier and the properties are reproducible. Among the different n-type dopants, doping with aluminium (Al), gallium (Ga) and indium (In) have been attempted by many groups using different deposition techniques [2,8–10] resulting in high quality ZnO thin films.

However, not much attention has been paid towards the preparation of ZnO thin film by thermal evaporation technique. This method is relatively simple and low cost procedure. The method does not require any catalyst or high temperature growth and the temperature of further oxidation of the film in thermal evaporation method is also moderate enough to be easily applied in thin film technology. The effect of annealing and the oxidation mechanism of as deposited ZnO thin films obtained by thermal evaporation technique have already been reported [11,12]. This work is an attempt to improve the electrical conductivity of thermally evaporated ZnO thin films by doping, without disturbing its transparency and structural properties significantly.

2. Experimental details

Zinc oxide thin films obtained in this study were prepared by thermal evaporation of a high quality ZnO powder (Alfa Aesar 99.99%) using tungsten boats. Soda lime glass slides were used as substrates and 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% of gallium oxide powder (99.9% Alfa Aesar) is evaporated maintaining other deposition parameters same as that of undoped films. Thickness of the films obtained was found out by gravimetric analysis and it is maintained to 200 nm in both the cases.

It is well known that during evaporation process ZnO powder decomposes in to zinc and atomic oxygen according to the kinetics of evaporation of ZnO and oxygen will be released as the primary by-product of the process [13]. 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 undoped and doped films were annealed at 300°C for 2 h for further oxidation [12]. During the process of annealing films will undergo oxidation and hence there will be an improvement in the stoichiometry. Thus all films turn transparent after annealing. There are reports, which prove the improvement in stoichiometry of thermally evaporated ZnO thin films after annealing [11,12,14]. Films were further subjected to detailed structural, optical and electrical characterization.

Structural characterization of the obtained ZnO thin films was studied by X-ray diffractometer using JEOL diffractometer with a scanning rate of 1°/min. The Scanning Electron Microscopy (SEM) studies to know the surface morphology of the films was performed with JEOL JSM 6380 system. 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. The electrical characterizations of the ZnO thin films were found out on coplanar structures consisting of two silver strips evaporated on the film surface. The measurements were

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carried out with computer assisted Keithley source meter (2400) setup.

3. Results and discussion

X-ray diffractograms of the films obtained in the undoped as well as in the doped state did not show any peak which confirms the amorphous nature of the films.

The scanning electron micrographs of the surface of the undoped and Ga2O3 doped films are shown Fig. 1, 2. It is found that all films have a smooth continuous and pinhole free microstructure and hence it is clear that there is no modification in the surface topography of the film due to doping.

Fig. 3 shows the transmittance spectra of undoped and gallium oxide doped zinc oxide thin films after annealing. From the spectra, it is confirmed that both undoped and doped films have transmittance of an average of 90% in the visible region of the electromagnetic radiation spectrum. This reveals that the transparency of the film is retained even after doping.

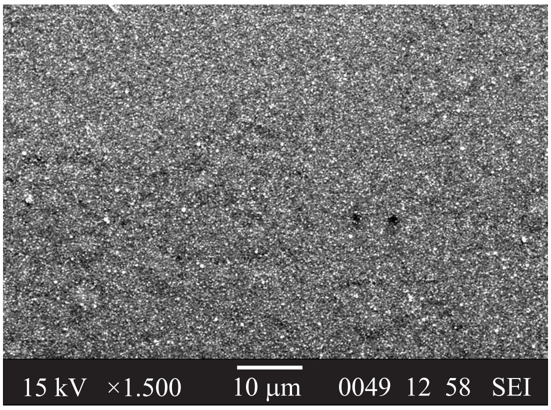

Figure 1. SEM image showing the surface topography of undoped ZnO thin film.

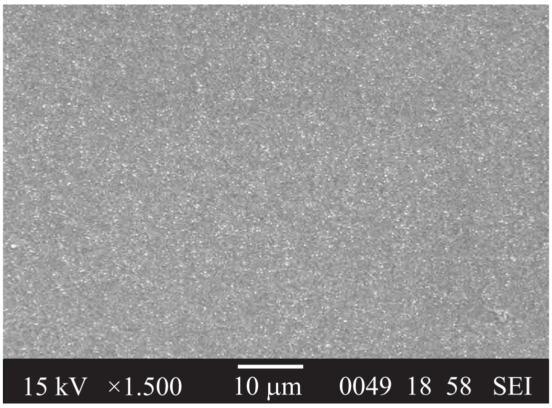

Figure 2. SEM image showing the surface topography of ZnO thin film after doping with 5% of Ga_2O_3.

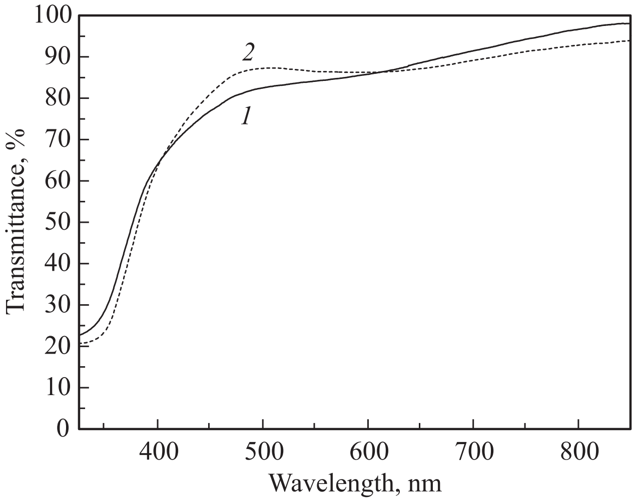

Figure 3. Transmittance spectra of undoped (*1*) and Ga_2O_3 doped (*2*) ZnO thin films.

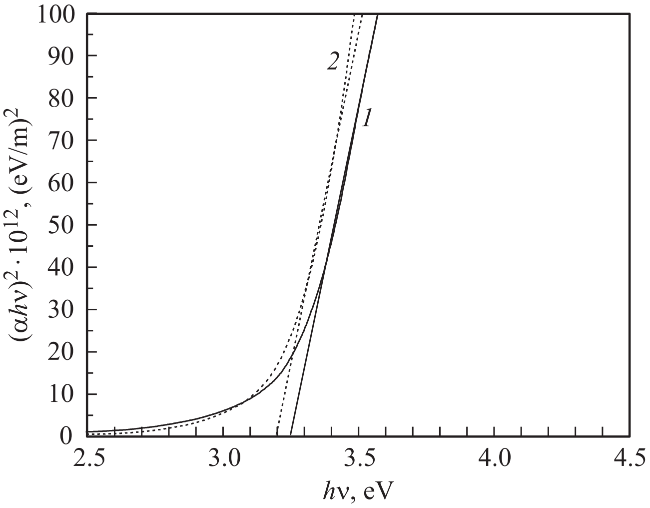

Figure 4. Plot $(\alpha h\nu)^2$ as a function of $(h\nu)$ for undoped (*1*) and Ga_2O_3 doped (*2*) ZnO thin films.

The optical energy gap E_g of films is estimated from optical measurements. Since ZnO is a direct band gap semiconductor allowed direct transitions can be assumed and the spectral dependence of the absorption coefficient, α can be described using equation [15].

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

where $h\nu$ — photon energy and B is a constant. The variation of $(\alpha h\nu)^2$ with $h\nu$ is plotted and the linear portion of the plot is extrapolated to zero to find the band gap of the film (Fig. 4). It is observed that the band gap of the undoped film is 3.25 eV and after doping with 5% of Ga_2O_3 the band gap of the film is reduced to 3.2 eV. This reduction in the band gap is due to the formation of additional levels below the conduction band.

The room temperature conductivity of the undoped film is found to be $90\,\Omega^{-1}\text{cm}^{-1}$. This is conductivity is conside-

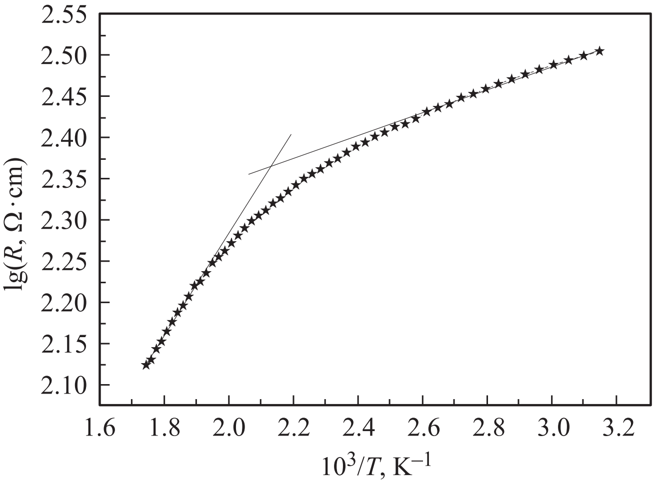

Figure 5. Logarithmic resistance profile with respect to reciprocal of temperature for Ga_2O_3 doped ZnO thin film.

rably high as compared to previously reported results on the conductivity of undoped ZnO thin films [5,16,17]. Oxygen vacancies present in the film even after annealing will act as the defects in the film and will play a major role in improving the conductivity of the films. In binary oxides like ZnO oxygen vacancies are responsible for the conduction electron carrier generation. The electron generation can be explained using Kröger–Vink notation in the equation [18].

$$O_O^X \to V_O^{\cdot\cdot} + 2e' + \frac{1}{2}O_2(g). \qquad (2)$$

According to equation (2), an oxygen anion escaping from the crystal structure ($\frac{1}{2}O_2$) from the occupied oxygen site creates a doubly ionized vacancy site ($V_O^{\cdot\cdot}$) and two free electron carriers. Thus, multiple carriers are created from a single defect and good *n*-type conductivity can be obtained. Hence, low resistivity at room temperature in ZnO thin film can be achieved by the creation of intrinsic donors by lattice defects such as oxygen vacancies. However, these intrinsically doped films will not be stable at ambient conditions [19]. At high temperature, these films will undergo oxidation and there will be a reduction in the oxygen vacancies and this leads to the significant increase in the film resistivity. Moreover, the resistivity of the intrinsically doped film can be reduced only up to 10^{-2}–10^{-3} $\Omega \cdot$ cm [19].

On doping ZnO thin film with 5% of Ga_2O_3, a great improvement in the conductivity of the film is observed. Doped films showed a room temperature conductivity of $8.7 \cdot 10^3\ \Omega^{-1}\mathrm{cm}^{-1}$. This considerably high improvement in electrical conductivity brought in by Ga_2O_3 doping can be explained as follows. When group III oxides like Ga_2O_3 are added to zinc oxide, it is assumed that group III dopant atoms will built into the zinc lattice sites spending additional electrons which are not required for the bonding to the conduction band according to the equation (3) [20]. These additional electrons will improve the conductivity of the film.

$$Ga_2O_3 \to 2Ga_{Zn} + 2e + \frac{1}{2}O_2. \qquad (3)$$

To calculate the activation energy, 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 film up to 300°C from room temperature. In this low temperature, extrinsic conduction predominates since ZnO has a wide band gap of the order of 3.3 eV. The semiconducting nature of the films follows the following relation [21].

$$R = R_0 \exp(E_a/k_B T), \qquad (4)$$

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 ($1/T$) is shown (Fig. 5). From the logarithmic resistance profile with respect to reciprocal of temperature, the thermal activation energy is calculated using the equation (5).

$$E_a = [2.303k_B(\text{slope})]/e, \qquad (5)$$

where e — magnitude of charge on electron.

In the graph (Fig. 5), lg$R$ verses $1/T$, for Ga_2O_3 doped ZnO thin film curve shows a linear behaviour in two regions. The first one from (1.7–2.1) 1/K and the other from (2.3–3.2) 1/K. In these two ranges the activation energy is proportional to the slope and gallium oxide doped ZnO thin film presents activation energy of 26 meV in the $1000(1/T)$ range (2.3–3.2 [1/K]) and another activation energy of 68 meV in the $1000(1/T)$ range (1.7–2 [1/K]). Basically, the electron concentration in ZnO thin film increases by gallium 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 [22].

4. Conclusions

We have used thermal evaporation method as a simple and low cost technique for the preparation of ZnO thin films. It is observed that the films obtained have a very high conductivity of $90\ \Omega^{-1}\ \mathrm{cm}^{-1}$ with a good transparency of more than 90% in the visible region. This considerably high conductivity in the undoped state of the film may be attributed to the presence of oxygen vacancies in the film, which act as intrinsic donors and improve the conductivity of the film. Doping of Ga_2O_3 in ZnO thin film leads to the greater improvement in the conductivity without much obvious change in the transmittance. The conductivity of doped films is found to be $8.7 \cdot 10^3\ \Omega^{-1}\mathrm{cm}^{-1}$ with a visible region transmittance of 90%. It is observed that the Ga_2O_3 doped ZnO thin film has an activation energy one at 68 meV and other at 26 meV bellow the conduction band. Thus Ga_2O_3 doped ZnO thin film with an excellent combination of transparency, conductivity and with smooth surface which is well suited for the application of transparent electrodes and flat panel displays, can be obtained by thermal evaporation technique.

References

[1] Y. Shigesato. In: *Hand book of transparent conductors*, ed. by S. Devid Ginley, Hideo Hosono, C. Devid Paine (Springer, N.Y., 2010), p. 161.
[2] Quan-Bao Ma, Zhi-Zhen Ye, Hai-Ping He, Li-Ping Zhu and Bing-Hui Zhao, Mater. Sci. Semicond. Process, **10**, (4–5) (2008).
[3] Minhong Jiang, Xinyu Liu, Hua Wang. Surf. Coat. Technol., **203**, 24 (2009).
[4] S.H. Jeong, S. Kho, D. Jung, S.B. Lee, J.H. Boo. Surf. Coat. Technol., 174–175 (2003).
[5] V. Craciun, J. Elders, J. Gardeniers, G.E. Ian, W. Boyd. Appl. Phys. Lett., **65**, 23 (1994).
[6] T. Prasada Rao, M.C. Santhosh Kumar. App. Surf. Sci., **258**, 8 (2009).
[7] Chien-Yie Tsay, Kai-Shiung Fan, Sih-Han Chen, Chia-Hao Tsai. J. Alloys Comp. **495**, 1 (2010).
[8] T. Prasada Rao, M.C. Santhosh Kumar. J. Alloys Comp. **506**, 2 (2010).
[9] A. Hafdallah, F. Yanineb, M.S. Aida, N. Attaf. J. Alloys Comp., **509**, 26 (2011).
[10] Changhyun Lee, Koengsu Lim, Jinsoo Song. Sol. Energy Mater. Sol. Cells. **43**, 1 (1996).
[11] S.A. Aly, N.Z. El Syed, M.A. Kaid, Vacuum, **61**, 1 (2001).
[12] M.S. Aida, E. Tomsella, J. Cellier, M. Jacquet, N. Bouhssira, S. Abed, A. Mosbah. Thin Sol. Films, **515**, 4 (2006).
[13] V. L'vov Boris, L. Valer Ugolkovb, F. Fedor Grekovc. Thermochim. Acta. **411**, 2 (2004).
[14] N. Bouhssira, S. Abed, E. Tomsella, J. Cellier, A. Mosbah, M.S. Aida, M. Jacquet. App. Surf. Sci., **252**, 15 (2006).
[15] U.P. Khairnar, D.S. Bhavasar, R.U. Vaidya, G.P. Bhavasar, Mater. Chem. Phys., 80, 2 (2003).
[16] A.N. Banerjee, C.K. Gosh, K.K. Chattopadhyay, Hideki Minoura, K. Ajay Sarkar, Atsuya Akiba, Atsushi Kamiya, Tamio Endo. Thin Solid Films, **496**, 1 (2006).
[17] G.G. Rusu, M. Rusu, Mahela Girtan. Superlattice Microst. **42**, (1-6) (2007).
[18] R. Kykyneshi, Jin Zeng, P. Devid Cann. In: *Hand book of transparent conductors*, ed. by S. Devid Ginley, Hideo Hosono, C. Devid Paine (Springer, N.Y., 2010), p. 173.
[19] K. Elmer. In: *Hand book of transparent conductors*, ed. by S. Devid Ginley, Hideo Hosono, C. Devid Paine (Springer, N.Y., 2010), p. 208.
[20] K. Elmer. In: *Hand book of transparent conductors*, ed. by S. Devid Ginley, Hideo Hosono, C. Devid Paine (Springer, N.Y., 2010), p. 210.
[21] S.M Sze. *Physics of Semiconductor Devices* (Wiely, N.Y., 2006).
[22] A.E. Jimenez-Gonzalez, J.A. Soto Urueta, R. Suraz-Parra. J. Cryst. Growth **192**, (3–4) (1998).

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