ZnO thin films by spray pyrolysis and its doping with Sb

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Abstract
Highly transparent ZnO thin films were prepared using spray pyrolysis of a solution containing Zn(OAc)2 and SbCl3 on glass substrates kept at 400 ºC. Further, these films were doped with Sb by in situ process by dissolving SbCl3 in the spray solution. Crystallographic structural analysis was done using X-ray diffractometer and elemental analysis was done using Auger electron spectrometer. Morphological characterization was done by atomic force microscopy. The UV-Vis transmittance measurements indicated that the films were 90% transparent in the visible region. The value of band gap energy calculated from UV-Vis characterization showed that undoped and Sb doped films have slightly different band-gap energies. The electrical resistivity measurements showed a substantial change in the resistance of the ZnO thin films due to Sb doping.

Keywords: Spray pyrolysis, ZnO, antimony doped ZnO

1. Introduction

Zinc oxide (ZnO) has been an extensively studied wide band gap semiconducting material [1]. ZnO in its bulk/thin film and nanostructure form have potential applications in LEDs, solar cells, flat panel displays and laser emission [1]. There are several reports, which describe the substantial changes in their electrical and optical properties due to doping. N-type doping is relatively easy compared to p-type doping for this material [1]. Doping with group III elements such as Al [2], Ga [3], and In [4] as substitutional elements of Zn by various methods were illustrated, and group VII elements such as Cl and I [5] were used as O substitutional elements to induce n-type conductivity. Spray pyrolysis is one of the low cost methods to prepare ZnO thin films with the added advantage of mixing the salt containing the dopant atoms with the precursor spray solution. ZnO thin films of 90 - 95 % transmittance were deposited on glass substrate at 490 ºC by spraying a solution containing zinc acetate [6]. At similar conditions, formation of polycrystalline ZnO thin films and a decrease in its resistivity with increase in substrate temperature were observed [7]. Microstructural changes in ZnO thin films formed using zinc acetate precursor [8, 9] and detailed electrical characterization of were discussed [10]. Preparation of ZnO thin films using zinc chloride solution and their doping with Sn or/and Al were also reported [11-14]. Luminescent properties of sprayed ZnO and ZnO:In thin films were investigated [15].

In the present work, we report the formation of ZnO thin films by spraying a solution containing $Zn(OAc)_2$ on glass substrates at 400 ^oC. Also, doping of these films with Sb by mixing $SbCl_3$ with the precursor solution is achieved. The thin films obtained were polycrystalline with transmittance as high as 90 % in the visible region. Analysis of X-ray diffraction patterns of the doped and undoped thin films showed the formation hexagonal ZnO phase. The elemental analysis by Auger spectroscopy indicated the presence of Zn, O and Sb in these thin films. Evaluation of optical band gap from UV-Vis transmittance data showed that band gap value was slightly decreased with doping. The electrical resistivity measurements revealed a substantial change in the resistance of the ZnO thin films due to Sb doping.

2. Experiment

The chemical reactants used were zinc acetate (Fermont), $SbCl_3$ (Fischer Scientific) and Ethanol (CTR). Substrates were corning glass slides. Compressed air was used as the carrier gas. For the preparation of ZnO thin films, zinc acetate salt was dissolved in minimum volume of water and then made up to 250 ml by adding ethanol. Zn molarity was varied as 0.02 to 0.1. The substrate temperature was 400 ºC. The thin films formed by spraying the solution containing 0.06 M Zinc were selected for doping with Sb. For doping, $SbCl_3$ was dissolved in the precursor solution of Zn with stirring. The amount of Sb was varied as 2 %, 4 % and 6 % of total Zn in the precursor solution. For the present

study, ZnO:Sb thin films formed with 2 % Sb were selected.

The thin films were characterized using various characterization techniques. X-ray diffraction patterns (XRD) of the thin films were recorded using Siemens D5000 diffractometer using CuKα radiation. The elemental analysis was done using Auger electron spectroscopy. The morphological studies were done using Atomic force microscopy (Q-Scope 3500) in contact mode. The optical absorbance of the films was measured using Perkin-Elmer UV-Vis spectrophotometer. Electrical resistivity measurements were carried using Keithley 6487 picoammeter/Voltage sourc e interfaced with a computer. The contacts used were two planar electrodes of 5 mm in length and 3 mm in separation using silver paint.

3. Results and discussion

ZnO thin films were formed by decomposition of zinc acetate on the substrates kept at 400 °C. The thickness of the films was estimated as ~ 150 nm by gravimetric method. Figure 1 shows the XRD patterns corresponding to the ZnO and ZnO:Sb thin films. Standard diffraction pattern (PDF #36-1451) for hexagonal ZnO is also given in the figure for comparison. In the pattern corresponding to ZnO film, all the peaks are coinciding with the standard lines. The maximum intensity peak in the experimental pattern corresponds to (100) plane. In the case of Sb doped films, all the peaks match with that of the standard pattern. The maximum intensity, (101) peak, coincides with that of the standard (004) plane, which is parallel to (002) is also present in the doped films. No peak corresponding to Sb_2O_3 is observed in the pattern. Sb doping in ZnO thin films retained its hexagonal structure except induced growth of (004) plane suppressing the (112) plane. From the width of the peaks, average particle size was calculated for both the doped and the undoped thin films using Debye-Scherrer's formula. The values were 14 nm and 11 nm respectively. Thus, Sb doping slightly increased the particle size.

Auger electron survey of Zn:Sb thin film without surface etching is given in figure 2. The presence of Zn, O and Sb are indicated. These elements are identified by their major Auger peaks corresponding the transitions viz; Zn1(ZnLMM), O1(KLL), Sb1(MNN). A weak signal of C noted as C1 corresponding to (C(KLL) transition is also marked in the figure. This can be from zinc acetate or from surface impurity. Approximate quantification is done using the differential peak strength and the sensitivity factors for corresponding elements. The percentages are 49.3, 33, 5.7 and 12 respectively for Zn, O, Sb and C.

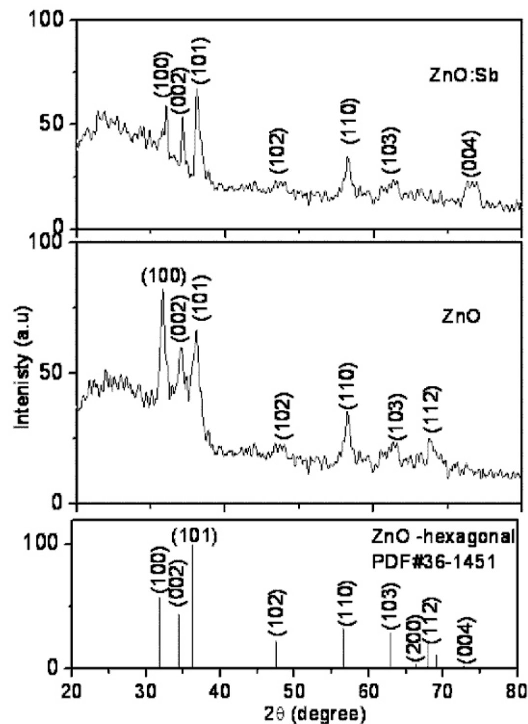

Figure 1. XRD patterns of ZnO and ZnO:Sb thin films

Morphological features of the doped and undoped films are given in the atomic force micrographs, figure 3. Nearly spherical grains are seen in both cases. In undoped thin films pinholes are present as observed in figure 3(a). However, the formation of pinholes is reduced by Sb doping as seen in figure 3(b). At the same time, there is a slight increase in the grain size due to doping which is in agreement with the XRD results.

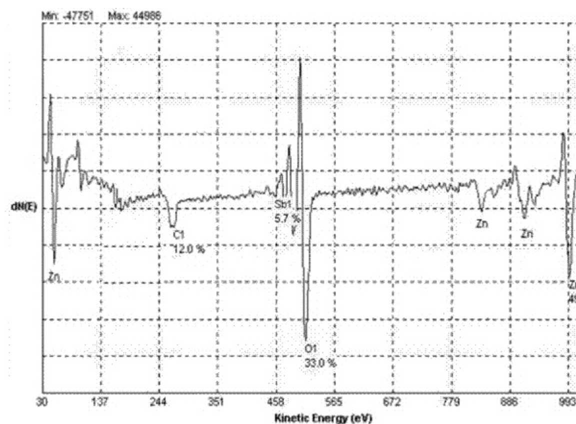

Figure 2. Auger survey for ZnO:Sb thin films

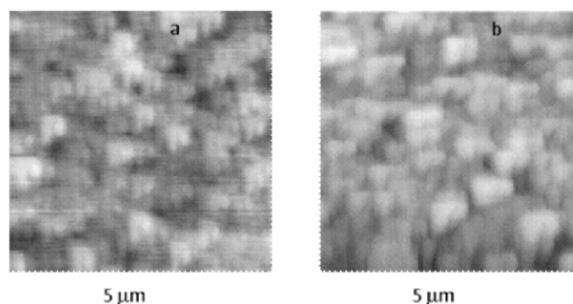

Figure 3. Atomic force micrographs for (a) ZnO and (b) ZnO:Sb thin films

Figure 4(a) shows optical transmittance (T) spectra of the doped and undoped films in the wavelength range of 350-900 nm. From the curves, nearly 90 % transmittance is observed in the case of undoped ZnO films. Due to doping transmittance is reduced to 80 %. From the spectral data, absorption spectra for both the films were generated using equation 1.

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \quad (1)$$

where, α is the absorption coefficient and t is the thickness of the film. From the spectra, the optical band gap of the thin films due to band-band transition is determined using the empirical relation (equation 2).

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where E_g is the optical band gap and n = 2, 1/2, 2/3 respectively for allowed direct, allowed indirect and forbidden direct transitions and A is a constant. We have chosen n = 2 which gives a good linear fit in the plot of $(\alpha h\nu)^2$ vs $h\nu$ as shown in figure 4 (b). The band gap values for the doped and undoped films are indicated in the figure and the respective values are 3.24 eV and 3.29 eV. The slight decrease in E_g can be attributed to the small increase in grain size for the Sb doped ZnO film. This result is in accordance with XRD analysis.

The electrical resistivity of the ZnO and ZnO:Sb thin films are evaluated from I-V characteristics of the films given in figure 5(a) and (b). The resistance (R) values were evaluated from the slope of the straight line graphs. By knowing the thickness (150 nm), the corresponding resistivity values were estimated. The values are of the order of 10^2 Ω cm and 10^7 Ω cm for ZnO:Sb and ZnO thin films respectively as indicated in the figure.

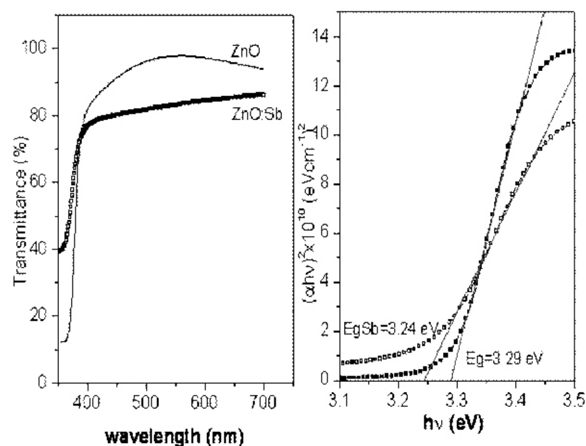

Figure 4. (a) Transmittance spectra (b) Evaluation of Eg for ZnO and ZnO:Sb thin films

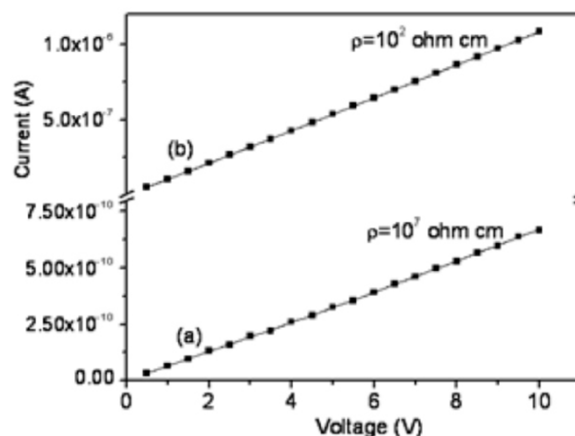

Figure 5. I-V characteristics for (a) ZnO and (b) ZnO:Sb thin films

Thus resistivity value of ZnO is significantly reduced by doping with 2 % Sb. By hot-probe technique, the doped films are found to be n-type. It was reported [1] that ZnO is naturally p-type semiconductor because of Zn interstitials or O vacancies. In the present case, the as-prepared ZnO films are nearly intrinsic. Doping of ZnO thin films with metals having higher valencies such as Al, Ga, In created shallow zinc substitutional defects [1-4] to form highly conducting films after doping. Hence, in the case of ZnO:Sb, the reduced resistivity can be attributed for the presence of substitutional defects of Sb_{Zn}.

4. Conclusions

ZnO thin films were prepared by spray pyrolysis using a solution of $Zn(OAc)_2$ on glass substrates at 400 °C. Also, ZnO:Sb thin films were obtained by

mixing $SbCl_3$ with the precursor solution for ZnO. The ZnO thin films formed were polycrystalline hexagonal structure with 90% transmittance in the visible region. After doping, the transmittance was reduced to 80 %. Auger spectroscopic analysis indicated the presence of Zn, O and Sb in these films. Optical band gap values were evaluated from UV-Vis transmittance data showed that band gap value for doped films was slightly lower than that of the undoped films. The electrical resistivity measurements showed a substantial change in the resistance of the ZnO thin films due to Sb doping. Thus Sb is a effective dopant for ZnO thin film which will be useful for various optoelectronic devices.

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6. References

1. Ozgur, U.; Alivov, Ya. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Dogan, S.; Avrutin, V.; Cho, S. J.; Morkoc, H. *J. Appl. Phys.* **2005** *98*, 041301.
2. Cooray, N. F.; Kushiya, K.; Fujimaki, A.; Okumura, D.; Sato, M.; Ooshita, M.; Yamase, O. *J. Appl. Phys.* **1999**, *38*, 6213.
3. Olvera de la L, M.; Maldonado, A. *Phys. Status Solidi A.* **2003**, *196*, 410.
4. Zironi, E. P.; Canetas-Ortega, J.; Gomez, H.; Maldonado, A.; Asomosa, R.; Palacios-Gomez, J. *Thin Solid Films* **1997**, *293*, 117.
5. Kato, H.; Sano, M.; Miyamoto, K.; Yao, T. *J. Cryst. Growth.* **2002**, *538*, *237-239*.
6. Peredins, D.; Gauckler, L. J. *J. Electroceramics* **2005**, *14*, 103.
7. Ashour, A.; Kaid, M. A.; El-Sayed, N. Z.; Ibrahim, A. A. *Appl. Surf. Sci.* **2006**, *252*, 7844.
8. Paraguay D., F.; Estrada L., W.; Acosta N., D. R.; Andrade, E.; Miki-Yoshida, M. *Thin Solid Films* **1999**, *350*, 192.
9. Van Heerden, J. L.; Swanepoel, R. *Thin Solid Films* **1997**, *299*, 72.
10. R. Ayouchi, D. Leinen, F. Martin, M. Gabas, E. Dalchiele, J. R. Ramos-Barrado, *Thin Solid Films* **2003**, *426*, 68.
11. Allah, F. K.; Abe, S. Y.; Nunez, C. M. ; Khelil, A. ; Cattin, L.; Morsli, M.; Bernede, J. C.; Bougrine, A.; del Valle, M. A.; Diaz, F. R. *Appl. Surf. Sci.* **2007**, *23*, 9241.
12. Mohammad, M. T.; Hashim, A. A.; Al-Maamory, M. H. *Mater. Chem. Phys.* **2006**, *99*, 382.
13. Ben Achour, Z.; Ktari, T.; Ouertani, B.; Touayar, O.; Bessais, B.; Ben Brahim, J. *Sens. Actuators, A* **2007**, *134*, 447.
14. Bougrine, A.; El Hichou, A.; Addou, M.; Ebothe, J.; Kachouane, A.; Troyon, M. *Mater. Chem. Phys.* **2003**, *80*, 438.
15. Kumar, P. M. R.; Kartha, C. S.; Vijayakumar, K. P.; Abe, T.; Kashiwaba, Y.; Singh, F.; Avasthi, D. K. *Semicond. Sci. Technol.* **2005**, *20*, 120.