

Aluminium doped zinc oxide films as a transparent conducting electrode for organic light emitting devices

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Aluminium (Al) doped Zinc Oxide (ZnO) films were deposited by sol gel spin coating method. Zinc acetate, aluminium nitride, lactic acid and ethanol were used as starting precursors. The films of aluminium doped ZnO were deposited on microscopic glass substrate at various atomic percentage of aluminium to investigate its effect on electrical and optical properties. The sheet resistance was altered with change in aluminium concentration. The minimum sheet resistance of 0.82 Mohm was obtained at 1.41 at% of Al. From the transmittance spectra, it was noticed that the average transmittance was declined for higher values of Al at%. The optical band gap energy was ~3.2 eV for undoped ZnO and was found to be shifted to ~3.39 eV for the sample having the lowest sheet resistance.

(Received April 7, 2008; accepted May 15, 2008)

Keywords: Aluminium zinc oxide, Sol gel, Sheet resistance

1. Introduction

Transparent conducting Oxides (TCO) are of major thrust in the research of semi-conducting materials due to their applicability in emerging organic and optoelectronics field and the nature of conductivity and transparency in the visible range [1]. Largely the doped and undoped TCO based on the Sn, Zn and In compounds were investigated. Indium tin oxide (ITO) was perhaps the most investigated TCO for various applications. However, indium is inadequate element on earth growing the cost of fabrication, as well as its toxic nature is hazardous to human and environment. For this purpose, new combinations of TCO were attempted which can give the optimum transparent and optical properties for the organic electronic devices. Now a day, the interest was shifted to the ZnO films in which electrical and transparent property can be altered by doping group III elements and VII elements [2]. Investigation has showed that aluminium doped Zinc oxide TCO films can fulfill the need as a transparent electrode for organic electronic devices [3]. Therefore it can be considered as the best candidate to replace the ITO in near future for organic electronics.

There are many techniques by which the doped ZnO films can be fabricated. It includes the pulsed laser deposition [4], spray pyrolysis [5], sputtering [6] and sol gel [7]. The sol gel process is more convenient, reducing the cost of fabrication process and its simplicity provides the efficient controlling on the doping concentration. Many authors have reported the aluminium doped ZnO thin films deposited by sol gel method [8-12]. Reports suggest that increasing the thickness can reduce the sheet resistance of the TCO film. This increase in thickness leads to the increase in the absorption coefficient of the film, which significantly reduces the quality of the TCO. The carrier density depending upon the atomic percentage

of doped element has major effect on the optical as well as its electrical properties.

Therefore, in this work, the study has been carried out to investigate the effect of Al doping in ZnO films. The undoped and Al doped ZnO films were deposited by spin coating method. The UV-Visible spectrophotometer characterization was carried out to determine transmittance spectra of the film. Using two-probe setup the sheet resistance was measured.

Following section of the paper explains experimental procedure for doping Aluminium in zinc oxide. The most significant results have been discussed thereafter. Finally, conclusions are highlighted.

2. Experimental procedure

The zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$], ethanol and lactic acid were used as the precursors. The thin films obtained using above precursors except aluminium nitrate nona-hydrate has been already reported for preparation of undoped ZnO [13]. In this process, the aluminium nitrate nonahydrate was used as the doping element. The zinc acetate and aluminium nitrate nonahydrate were mixed together in absolute ethanol. The mixture was vigorously stirred on hot plate with magnetic stirrer maintained at ~60°C and the lactic acid was added drop wise in the solution. After stirring for half an hour the solution became fully transparent. The solutions were prepared for the various at. % of aluminium. In this experiment, zinc acetate molar concentration was kept 0.4 mole/litre. The obtained solutions were used to deposit the thin films. The commercially available microscopic glass slides were used as substrate to deposit the films. The undoped and doped ZnO films were deposited on the glass by the spin coater maintained at constant speed. It was ensured that the

constant thickness of coating can be attained per coat. The samples were coated repeatedly for the six times. After each coating the sample was heat treated at 250 °C for one minute and cooled down at room temperature before applying new coat. This preheat treatment is necessary for evaporation of the organic group contents present in the films. These deposited samples were annealed at 400 °C temperature in open air for one hour to obtain the crystalline undoped and Al doped ZnO films.

The deposited samples were characterized by shimadzu-2000 UV-VIS spectrophotometer to determine the transmittance spectra. Uncoated glass substrate was used as a reference substrate in spectrophotometer. The electrical property was studied by two-probe setup. The distance between the probes in setup was 1.22 mm. The sheet area of 1 cm² was used for the measurement of resistance of deposited samples.

3. Results and discussion

To explore the potential of Al doped zinc oxide as transparent conducting electrodes for the organic light emitting devices, transmission spectra, sheet resistance and absorption coefficient were investigated. Figure 1(a) shows the transmittance spectra obtained for the undoped and Al doped ZnO films.

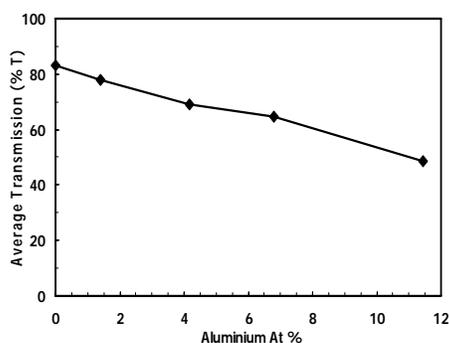
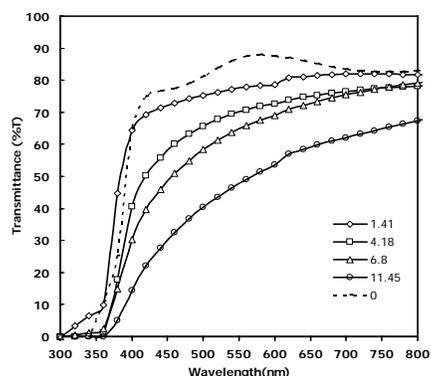


Fig. 1. (a) Transmittance spectra of undoped and Al doped ZnO films at various Al% (b) Average transmittance spectra

The undoped ZnO film was showing the oscillating nature in spectra suggesting excellent adhesion and consequent interference in layers of the film on glass substrate. The effect of Al doping can be clearly seen on the transmittance of the films. The transmittance spectra of films were declined for the increased doping of Al at%. For comparing the effect of Al doping on transmittance the average transmittance was determined as shown in figure 1(b) in the visible wavelength range. The average transmittance of undoped ZnO film was found to be higher than the Al doped films [14]. The clear evidence of shift in the optical band gap of undoped ZnO (~3.2 eV) and 1.14 at.% Al doped ZnO films (~3.39) were observed by deducing absorption coefficient as shown in Fig. 2 by the normally used linear extrapolated method.

The graph was plotted for the measured sheet resistance of deposited undoped and Al doped ZnO films as depicted in Fig. 2.

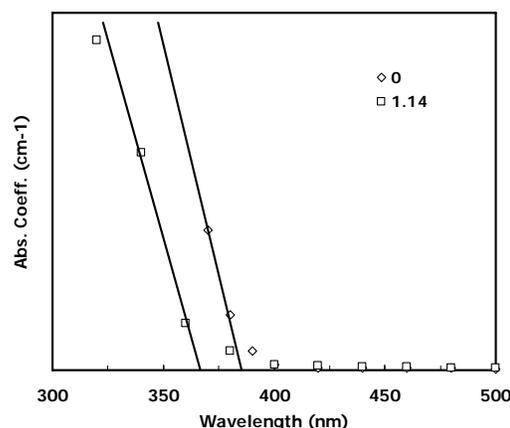


Fig. 2. Absorption coefficient Vs Wavelength

The sheet resistance of undoped ZnO was 6.2 MΩ/□ and reduced up to 2.87 MΩ/□ for maximum Al%. The minimum sheet resistance of 0.82 MΩ/□ was obtained at 1.41 at.% of Al doping. The obtained results are in close agreement to the sheet resistance values reported by Hosono et al. for the micro/nano porous Al doped ZnO films deposited by chemical bath deposition [15]. The electrical resistivity obtained in these films is attributed to the porous structure associated with the sol gel process. The low sheet resistance obtained at 1.41 at%, is due to the Al substitution at Zn in the grain boundaries leaving additional electrons acting as a donor. At the higher doping concentration, segregation of Al takes place, which results in the increase of resistance of deposited films. It was observed here, that there is a significant effect of Al doping on the electrical and optical properties of the films.

This behavior of the transmittance and sheet resistance can be well explained by the doping mechanism of Al in ZnO. The maximum thermodynamic solubility of Al in ZnO is up to 2-3 at % [16]. From figure 1(b), it was seen that the absorbance edge of 1.14 at% Al doped ZnO shifts to lower wavelength resulting optical band gap energy of ~3.39 eV, while for >1.14 Al at. % absorbance

edge shifts towards the visible wavelength range. At 1.14 at.% Al doped ZnO films, the doping of Al solubility is larger, which in turn gives the rise in the carrier concentration and causes the Burstein-Moss band edge shift. It shows that the Al was doped into ZnO crystal lattices. It results in lowering of the resistivity of Al doped ZnO film. Now, for the greater Al doping concentration >1.14 at %, the doping of Al was not took place properly at the ZnO grains due to the thermodynamic solubility limit. The scattering effect of the carriers occurs in the ZnO grains, resulting in the shifting of absorbance edge at visible wavelengths. This scattering of the electrons affect the mobility which in turn increases the resistivity of the AlZnO films as shown in Fig. 3.

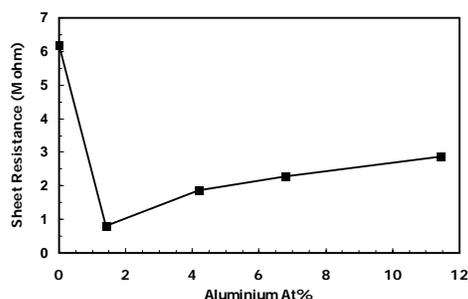


Fig. 3. Sheet resistance of undoped and Al doped ZnO films at various At%

4. Conclusion

Al doped ZnO films were successfully deposited by sol gel method at various at%. The significant effect of Al doping was observed on the transmittance of the Al doped films. The increased at.% of aluminium in ZnO results in decreasing of the average transmittance of the films. The minimum sheet resistance of $0.82 \text{ M}\Omega/\square$ was obtained at 1.41 at% doping concentration, while $6.2 \text{ M}\Omega/\square$ was obtained for undoped ZnO film using ethanolic solution. We conclude that by optimizing process parameters, transmittance and conductivity of Al doped ZnO films can be controlled for exploring their potential in organic light emitting devices.

References

- [1] R. Gordon, Materials Research Science Bulletin **52** (2000)
- [2] U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogav, V. Avrutin, J. Appl. Phys. **98**, 041301 (2005)
- [3] S. H K. Park, J. I. Lee, C. S. Hwang and H. Y. Chu, Jap. J. Appl. Phys. **44** (7), L242 (2005)
- [4] R.K. Shukla, A. Srivastava, A. Srivastava and K.C. Dubey, J. Crystal Growth, **294(2)**, 427 (2006)

- [5] A. E. Hichou, M. Addou, A. Bougrine, R. Dounia, J. Ebothe, M. Tryoyon, M. Amrani, Material chemistry and physics **83**, 43 (2004)
- [6] B. Y Oh, M. C. Jeong, W. Lee and J. M. Myoung, J. Crystal Growth, **274**, 453 (2005)
- [7] M. P. Bhole, D. S. Patil, Modern Physics letters B. **22**, 685 (2008)
- [8] Keh-moh Lin, Paijay Tsai, Thin Solid Films **15**, 8601 (2007)
- [9] M. Zhu, H. Huang, J. Gong, C. Sun, J. Appl. Phys. **102**, 043106 (2007)
- [10] T. Schuler and M. A. Aegerter, Thin Solid Films **30**, 125 (1999)
- [11] M. Ohyama, H. Kozuka, T. Yoko, J. Am. Ceram. Soc. **81(6)**, 1622 (1998)
- [12] R. B. H. Tahar, N. B. H. Tahar, J. Am. Ceram. Soc. **88** (7), 1725 (2005)
- [13] M. P. Bhole, D. S. Patil, Opto. Adv. Mater- RC, **1** (12), 672 (2007)
- [14] S. H. Jeong, B. N. Park, D. G. Yoo, J. H. Boo, J. Korean Phy. Soc. **50** (3), 622 (2007)
- [15] E. Hosono, S. Fujihara, T. Kimura, J. Mater. Chem. **14**, 881 (2004)
- [16] J. G. Lu, Z. Z. Ye, Y. J. Zeng, L. P. Zhu, L. Wang, J. Yuan, B. H. Zao, X. Jiang, J. Appl. Phys. **100**, 073714 (2006)

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