Journal of Physical Sciences, Vol. 12, 2008, 221-229

Preparation of Al-doped ZnO (AZO) Thin Film by SILAR

S. Mondal, K. P. Kanta and P. Mitra
Department of Physics
The University of Burdwan,
Golapbag, Burdwan – 713104, West Bengal
e-mail: mitrapartha1@rediffmail.com; bu_pm@yahoo.com

Received April 17, 2008; accepted October 1, 2008

ABSTRACT

Aluminum doped zinc oxide (AZO) thin film was deposited on microscopic glass substrate following a chemical technique called successive ion layer adsorption and reaction (SILAR). The technique involves multiple dipping of the substrate in an aqueous solution of sodium zincate kept at room temperature and deionized water kept near boiling point. Al doping was found to increase the film growth rate. It was approximately 0.20 μm/mole/dipping for ZnO film and 0.22 μm/mole/dipping for AZO film. Structural characterization by X-ray diffraction (XRD) technique confirmed incorporation of aluminum in ZnO lattice. The c-axis orientation was significantly enhanced due to Al incorporation which was revealed from marked increase of (002) peak intensity compared to other peaks of hexagonal ZnO. The cross sectional view in SEM (Scanning electron micrograph) also reveals growth of large crystallites perpendicular to the substrate. The resistance of the film decreased about one order in magnitude due to Al doping. The activation barrier value of 0.31 eV for ZnO film was however found to be unaffected due to aluminum incorporation.

***Keywords:** AZO, Thin films, SILAR*

1. Introduction

The synthesis and characterization of zinc oxide and doped zinc oxide via different techniques have attracted considerable attention due to their application prospects in the development of materials area. ZnO have high transparency in the visible and near-ultraviolet spectral regions, wide conductivity range and conductivity changes under photoreduction/oxidation condition [1]. Accordingly this binary compound has wide applications in chemical sensors, heterojunction solar cells, electrophotography, surface acoustic wave devices, conductive transparent conductors and many others. However, pure ZnO thin films lack stability in terms of thermal edging in air or corrosive environments [2]. Therefore polycrystalline ZnO films have been doped with group II and group III metal ions such as indium (In), aluminum (Al), gallium (Ga), copper (Cu), cadmium (Cd) etc. to enhance their structural, optical and electrical properties [3]. Doping is particularly done to get high transparency, stability and high conductivity. Aluminium doping is particularly suitable for this purpose. Aluminium doped ZnO (AZO) thin films have high transmittance in the visible region, and a low resistivity, and the optical band gap can be controlled by using Al doping amount [4]. Accordingly they have got potential applications in solar cells, antistatic coatings, solid-state display devices, optical coatings, heaters, defrosters, chemical sensors etc. [4-5].

Different physical and chemical techniques have been employed for aluminum incorporation in ZnO. These include dc and rf magnetron sputtering [1, 6], pulsed laser ablation [7], chemical vapor deposition [5], chemical beam deposition [8], sol-gel [9], electroless technique [10], spray pyrolysis [11] among others. The conventional physical techniques generally produce good quality transparent films. However they are very expensive and are difficult to carry out in the industrial level. Chemical deposition techniques, on the other hand, are relatively low cost processes and can be easily scaled up for industrial applications. Since the last two decades, chemical techniques have come out to be a good alternative for material preparation in thin film form.

Among various chemical methods employed so far to deposit AZO films, spray pyrolysis is a high temperature process and choice of suitable precursor solution is often not convenient. Sol-gel requires costly chemicals and electroless deposition is characterized with poor coverage. One of the less used and less studied chemical techniques is successive ionic layer adsorption and reaction (SILAR). The process can be carried out on any kind of substrate and the thickness can be easily controlled. Thus both thin and thick films can be prepared by this method.

The technique of SILAR is often termed as modified chemical bath deposition. In chemical bath deposition (CBD) method, deposition of thin films occurs due to substrate maintained in contact with dilute chemical bath. The film formation on substrate takes place when ionic product (IP) exceeds solubility product (SP). In SILAR technique, thin films are obtained by immersing the substrate into separately placed cationic and anionic precursors for reaction at chosen temperatures. Between every immersion it is rinsed in distilled water or deionised water and the rinsing time is important for ionic layer formation. For ZnO thin film deposition, the process was originally reported as multiple chemical dipping technique by Ristov et al. [12]. It was ascribed with the name SILAR by Nicolau et al. [13] since it involves adsorption of a layer of complex ion on the substrate followed by reaction of the adsorbed ion layer. The advantages of this method are its simplicity of working principal and low cost of apparatus. Since in SILAR technique, the deposition is carried out in ambient air, the microstructure of the SILAR deposited films are expected to be different from sophisticated physical techniques where the deposition is carried out in vacuum. They are expected to have different properties from other chemical techniques as well.

Earlier we reported the preparation of ZnO thin films by this technique from sodium zincate and ammonium zincate baths [14-15]. The aim of the present work was to promote interest in the SILAR method as applied to AZO thin films. To the best of our knowledge, for the first time an attempt was made for the preparation of AZO films by SILAR. For aluminium doping, sodium zincate solution was impurified with anhydrous aluminium chloride ($AlCl_3$). The concentration of Al was intentionally chosen to be large (7 at.%) so that the effects of Al (if incorporated in the ZnO lattice) can be easily detected.

2. Experimental

Deposition of ZnO and AZO film was carried out from 0.125M sodium zincate (Na_2ZnO_2) solution and hot water bath. Sodium zincate bath was prepared by adding sodium hydroxide (NaOH) in zinc sulphate ($ZnSO_4.7H_2O$ solution. The pH of the zincate solution was 11.60. Aluminium doping was carried out by adding anhydrous aluminium chloride ($AlCl_3$) in sodium zincate bath. The doping concentration was 7 at.% and this was found to be the maximum amount of Al doping possible in Na_2ZnO_2 bath. Further addition of $AlCl_3$ results in precipitate in the zincate solution. Film deposition was carried out by alternatively dipping a precleaned microscopic glass slide substrate in zincate bath kept at room temperature and hot water bath maintained at ~96-98°C. One set of dipping involves dipping in zincate bath for two (2) seconds and two (2) seconds in hot water bath. 200 dipping were performed for the present experiment.

The measurement of film thickness was carried out using gravimetry technique [16]. The method involves measuring the weight change of the doped ZnO film formed on the substrate due to film deposition and taking the theoretical density of ZnO. X-ray diffraction (XRD) with CuK_α radiation (λ=1.5418 Å) was used for structural characterization and phase identification of ZnO and AZO films in a Philips PW 1830 XRD-system. Scanning electron microscopy (SEM) was used to illustrate the formation of crystallites on the film surface.

The electrical characterization of the films was carried out in a tube furnace by monitoring the variation of electrical resistance (R) as a function of temperature (T) using conventional DC two-probe technique. The range of temperature investigated was 380-480 K with a control accuracy of (±)1 K. Approximately 20 mm long silver (Ag) contacts, separated by 5 mm, were made on ZnO films (30 mm× 25 mm) for electrical measurements. The width of the electrodes was approximately 1 mm. The conducting paste was cured at 200°C for this purpose. The resistivity ρ was determined from the relation $\rho = \frac{RL}{A}$, where L is the distance between two silver electrodes and A is the area, which is the product of length of the electrodes and thickness of the film.

3. Results and discussions

3.1 Film thickness

The measured film thickness was approximately 5.0 μm for undoped film and 5.5 μm for Al-doped films for 200 dipping. The film growth rate was 0.20 μm per dipping per mole for undoped film and 0.22 μm per dipping per mole for AZO film. Thus the result clearly indicates that aluminium incorporation promotes film growth rate.

The gravimetry method of film thickness determination has some limitations because of non-uniformity, porosity and edge tapering effects in the chemically deposited films with porous microstructure. The actual film density is lower than the theoretical density and the thickness measured using theoretical density is less than the actual thickness [15]. However, this error does not affect the comparative data of measured film thickness.

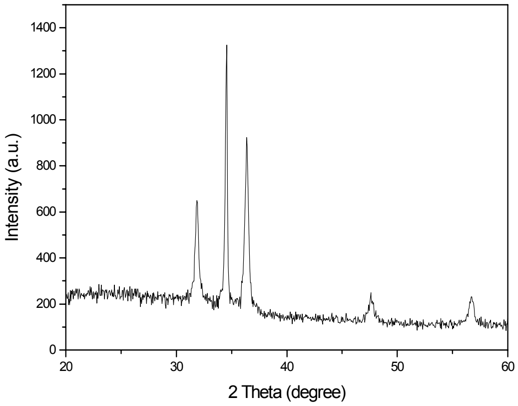

Figure 1: XRD pattern of undoped ZnO film

3.2 Structural Characterization

Figure 1 shows the X-ray diffraction (XRD) pattern of the 5.0 μm thick ZnO film deposited from sodium zincate bath. The film was annealed at 200°C in air prior to structural characterization. The material was scanned in the range 20-60°. Figure shows the plot of intensity (in arbitrary unit) against 2θ, where θ is the angle of incidence of X-ray beam. It is seen from Figure 1, the (002) peak appears with maximum intensity at 34.55°. The other peaks at 31.85°, 36.35°, 47.6° and 56.85° can be associated with (100), (101), (102) and (110) peaks of ZnO, as is expected for hexagonal ZnO structure [15]. The strong preferred c-axis orientation is evident from the figure.

Table-1

Miller indices	Relative Intensity of peaks for 150°C heat treated Zinc oxide film	Relative Intensity of peaks for 150°C heat treated AZO film	Relative Intensity of peaks for 400°C heat treated AZO film
(100)	45	26	27
(002)	100	100	100
(101)	70	42	42
(102)	19	12	13
(101)	17	10	10

Figure 2, on the other hand, shows the XRD pattern of AZO film. The figure indicates clearly that Al-doping promotes c-axis orientation. Figure 3 shows the pattern of the AZO film heat treated at 400°C for 1 hour. Heating at 400°C did not produce any modification in the structural orientation. The invariance in structure indicates that incorporation of aluminium was complete after 200°C heat treatment.

The location of the diffraction pattern peaks is shifted slightly to the high diffraction angle. Table 1 shows the miller indices of the planes and the relative intensity of the peaks for ZnO and aluminium doped ZnO films. It is evident that aluminium doping increases the intensity of (002) peak and decreases the intensity of all other peaks. No metallic Al characteristic peak was observed. This may be due to Al replacing zinc substitutionally in the lattice or aluminum segregation to the non-crystalline regions in the grain boundary. From the present experiment, we cannot conclude the amount of Al incorporation in the lattice. Suchea et al. [1] reported for sputtered films, there is an optimum doping level (~4 at.%) after which Al atoms don't go the lattice. Further experiments are required for drawing any conclusion for the present case of SILAR deposited films.

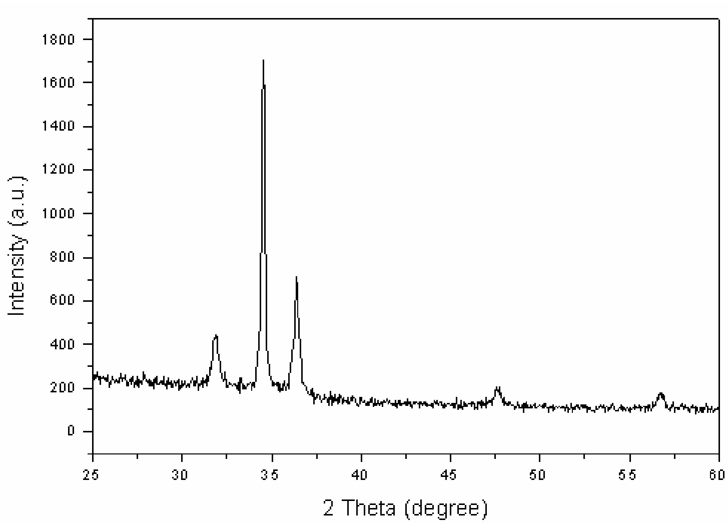

Figure 2: XRD pattern of 7% Al-doped ZnO film treated at 200°C

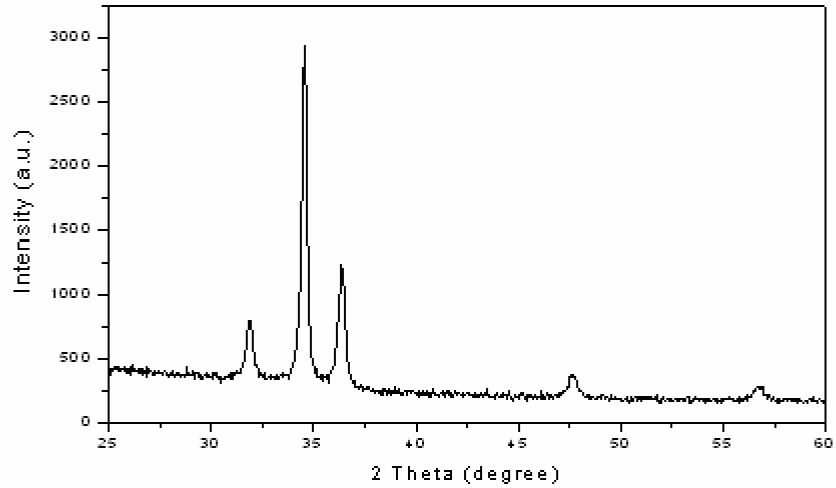

Figure 3: XRD pattern of heat treated (400°C, 1 hr.) Al-doped ZnO film

Scanning electron microscopy is a convenient method for studying the microstructure of thin films. The microstructure ZnO film on glass substrate is shown in figure 4. The polycrystalline and porous nature is revealed from the micrograph. The SEM photograph clearly illustrates the formation of sub-micrometer crystallites distributed more or less uniformly over the surface. Low deposition temperature in SILAR possibly results in large crystallites. results in large particle size. Although no cracks could be detected, some holes indicating porosity is present. Agglomeration of small crystallites also seems to be present in certain regions on the film surface. Figure 5 shows SEM of the AZO film. The cross-sectional view presented in the figure clearly indicates strongly oriented crystallites perpendicular to the substrate. Crystallite sizes were significantly increased due to Al incorporation.

Figure 4: SEM picture of ZnO film on glass

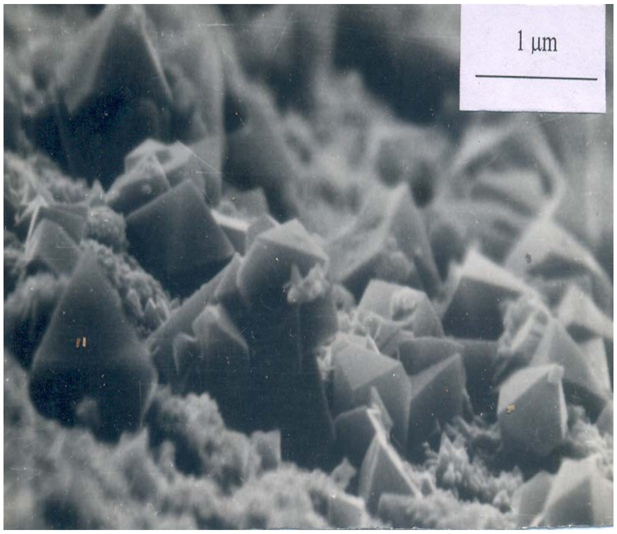

Figure 5: SEM picture of AZO film on glass (cross sectional view)

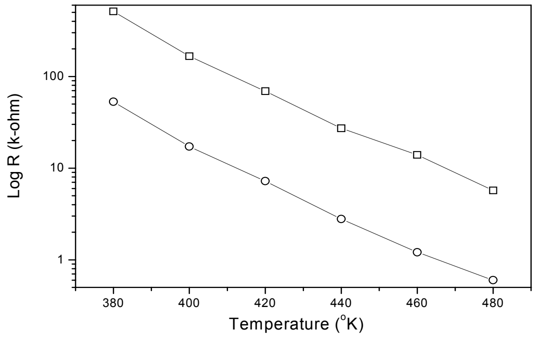

Figure 6: Variation of electrical resistance of ZnO and AZO film

3.3. Electrical resistance vs. temperature for ZnO and Al-ZnO films

The dark electrical resistance measurement was carried out in the temperature range 380-480K using the DC two-point probe method. Figure 6 shows the variation of resistance with temperature. In the figure, lnR (in kilo-ohms) is plotted against temperature. The decrease in resistance with increasing temperature following semiconducting behaviour of ZnO is observed.

The activation energy was determined by using the equation

$$R = R_o e^{E_a/kT} \tag{2}$$

where R is the resistance at temperature T, R_o is a constant, E_a is the activation energy and k is the Boltzmann constant

The value of activation energy is 0.31 eV for both undoped and AZO films. An activation barrier value of 0.3 eV for ZnO film was reported earlier [15]. Thus there is no change activation barrier value due to doping. However the decrease of resistance by approximately one order in the entire temperature range studied shows that aluminum atoms are incorporated into the ZnO lattice and contributes conduction electrons according to the equation

$$Al^{3+} \rightarrow Al^{2+} + e \tag{3}$$

Al^{2+} goes into ZnO lattice and the electron is free to contribute to electrical conduction.

The value of effective density of conduction electrons (n_{eff}) can be calculated from the equation [15]:

$$\sigma = n_{eff} e \mu$$

where $\sigma = \frac{1}{\rho}$ is the electrical conductivity, e is the electronic charge and μ is the mobility. As has been already mentioned that the resistivity ρ is determined form $\rho = \frac{RL}{A}$. Here R is the measured resistance, $L \cong 5$ mm. The area A is the product of length of the electrodes ($\cong 20$ mm) and thickness of the film ($\cong 5$ μm). From our present results, the value of n_{eff} comes out to be of the order of 10^{13} /cm^3 at around 380K for ZnO film. For AZO film it is of the order of 10^{14} /cm^3 at 380K. While calculating n_{eff}, the mobility value was assumed to be constant and equal to 20 cm^2 Vs^{-1} i e. temperature dependence of mobility was not taken into account. This will introduce only a small error in the calculation and will not affect the order.

4. Conclusions

The major conclusions of the present work are as follows:

a) Aluminium could be successsfully incorporated in ZnO thin film by SILAR technique. The concentration of Al was intentionally chosen to be large (7 at.%) so that the effects of Al can be easily detected. It may be possible to try still lower concentrations. Experiments in these directions are in progress. Optimisation of Al incorporation can give ZnO thin films with improved properties.

b) An analysis of the results presented here indicates that Al incorporation promotes growth rate and gives rise to highly c-axis oriented crystallites. Variation of Al incorporation will help to explain these phenomena. The objective of the present work was to check whether Al could be incorporated by a simple low cost chemical technique.

c) Al incorporation decreases the resistance by approximately one order in the temperature range studied. However, it does not affect the value of activation barrier.

Acknowledgement. The authors acknowledge DSA III, dept. of Physics, for providing the instrumental facilities for carrying out the work.

REFERENCES

1. M. Suchea, S. Christoulakis, N. Katsarakis, T. Kitsopoulos and G. Kiriakidis, *Comparative study of zinc oxide and aluminium doped zinc oxide transparent thin films by direct current magnetron sputtering*, Thin Solid Films 515 (2007), 6562-6566.
2. A. E. Jimenez-Gonzalez, *Modification of ZnO Thin Films by Ni, Cu, and Cd doping*, Journal of Solid-State Chemistry 28 (1997), 176-180.

3. Y. Cao, L. Miao, S. Tanemura, M. Tanemura, Y. Kuno, Y. Hayashi and Y. Mori, *Optical properties of Indium-doped ZnO films*, J. J. Appl. Phys. 45 (2006), 1623-1628.
4. S. H. Jeong, B. N. Park, D. G. Yoo and J. H. Boo, *Al-ZnO thin films as transparent conducting oxides: Synthesis, Characterization and Application tests*, Journal of the Korean Physical Society 50 (2007), 622-625.
5. J. Nishino, S. Ohshio and K. Kamata, *Preparation of Aluminum-Doped Zinc Oxide Films by a Normal-Pressure CVD Method,* J. Am. Ceram. Soc. 75 (1992), 3469-3472.
6. Y. E. Lee, Y. J. Kim and H. J. Kim, *Thickness dependence of microstructural evolution of ZnO films deposited by rf magnetron sputtering*, J. Mater. Res. 13 (1998), 1260-1265.
7. V. Srikant, V. Sergo and D. R. Clarke, *Epitaxial Aluminum-doped zinc oxide thin films on Sapphire:II, Defect equilibria and electrical properties*, J. Am. Ceram. Soc. 78 (1995), 1935-1939.
8. H. Sato, T. Minami, S. Takata, T. Miyata and M. Ishii, *Low temperature preparation of transparent conducting ZnO:Al thin films by chemical beam deposition*, Thin Solid films 236 (1993), 14-19.
9. M. Ohyama, Sol-Gel preparation of transparent and conductive Aluminum-doped zinc oxide films with highly preferential crystal orientation, J. Am. Ceram. Soc. 81 (1998), 1622-1632.
10. D. Raviendra and J. K. Sharma, *Electroless deposition of cadmium stannate, zinc oxide and aluminum-doped zinc oxide films*, J. Appl. Phys. 58 (1985), 838-844.
11. A. F. Aktaruzzaman, G. L. Sharma, L. K. Malhotra, *Electrical, optical and annealing characteristics of ZnO-Al films Prepared by spray pyrolysis,* Thin Solid Films, 198 (1991), 67-74.
12. M. Ristov, G. J. Sinadinovski, I. Grozdanov and M. Mitreski, *Chemical deposition of ZnO films*, Thin Solid Films 149 (1987), 65-71.
13. Y. F. Nicolau and J. C. Menard, Growth of Z NS, CdS and ZnO thin films by SILAR, J. Cryst. Growth, 92 (1988), 128-132.
14. P. Mitra and H. S. Maiti, *A wet-chemical process to form palladium oxide sensitiser layer on thin film zinc oxide based LPG sensor*, Sensors and Actuators 97 (2204), 49-58.
15. P. Mitra and J. Khan, *Chemical deposition of ZnO films from ammonium zincate bath*, Materials Chemistry and Physics 98 (2006), 279-284.
16. S. Mondal and P. Mitra, *Preparation of nanocrystalline SnS thin film by SILAR*, Accepted for publication in Material Science research India, 5 (2008).