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Studies on Variations in Textured Grain Growth in ZnO Nano Thin Films by Aluminium and Iodine Doping†

DEEPU THOMAS[1,2,*], SUNIL C. VATTAPPALAM[2], SUNNY MATHEW[2] and SIMON AUGUSTINE[2]

[1]Research and Development Centre, Bharathiar University, Coimbatore-641 046, India
[2]Department of Physics, St. Thomas College, Pala, Kottayam-686 574, India

*Corresponding author: Fax: +91 4822 216313; E-mail: deepuskariankal@gmail.com

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ZnO thin films were prepared by successive ionic layer adsorption reaction (SILAR) method. The variations in the textured grain growth along c-axis in the aluminium doped and iodine doped thin films were studied. Textured grain growth of the samples was measured by using an orientation index (O.I.), which is the ratio of the intensities of (002) reflection (2θ = 34º) to (101) reflection (2θ = 36º) in the XRD patterns. From the studies following conclusions were drawn. Textured grain growth in ZnO thin films is enhanced by aluminium and iodine doping. When the oriented grain growth increases, crystallinity of the thin film improves, resistance and band gap decreases. A possible mechanism for the textured grain growth is also investigated. It is inferred that the creation of defects are responsible for the enhanced textured grain growth in ZnO thin films by aluminium and iodine doping.

Key Words: ZnO thin film, SILAR method, Textured grain growth, Al and I-doping.

INTRODUCTION

The study of ZnO material has attracted much interest due to its wide band gap energy (*ca.* 3.3 eV) and large exciton binding energy (60 meV). The band gap energy of ZnO is almost similar to GaN (3.4 eV) which has been used for the manufacture of ultraviolet, blue, green and recently white light emitting diodes[1-3]. As a wide and direct band gap semiconductor, nanostructred ZnO thin films have attracted more attention in optoelectronic devices[4]. The transparent conductive oxide (TCO) electrodes using Al-doped ZnO have attracted much attention as a powerful candidate material for ITO transparent electrodes[5]. ZnO thin films have attracted considerable attention because they can be tailored to attain high electrical conductivity, high infrared reflectance and high visible transmittance by applying different techniques[6-9]. Different methods have been applied to obtain ZnO thin films. These include magnetron sputtering[7], chemical bath deposition[10], sol-gel[11], spray pyrolysis[12], *etc*. Chemical deposition techniques are relatively low cost processes and can be easily scaled up for industrial applications. Among the thin films deposition methods, double dip technique from aqueous solutions is the simplest and the most economical one. Double dip method, otherwise called SILAR method, (successive immersion layer adsorption reaction)[6,13,14] also offers the opportunity of doping the host ions with impurities on different kinds, shapes and sizes on substrates with ease. Zinc oxide crystallites with preferential grain growth along c-axis are desirables for applications such as UV diode lasers acousto-optic devices[4], *etc*. There are reports of enhanced oriented grain growth in ZnO thin films by doping and annealing. Controllable *n*-type doping is easily achieved by substituting Zn with group-III elements such as Al[5,6] or substituting oxygen with group-VII elements such as iodine[14,15].

In course of the present investigations, textured grain growth in aluminium and iodine doped samples was studied. A possible mechanism for the textured grain growth is also investigated.

EXPERIMENTAL

ZnO thin films were prepared by successive ionic layer adsorption reaction (SILAR) method, in which, the ZnO thin film was coated on a glass substrate (26 × 76 mm) by alternately dipping it in a sodium zincate bath at room temperature and then in hot water maintained at 90-95 ºC. Rostov *et al.*[16] had already used this method for preparing Cu_2O thin films and Chandramohan *et al.* for ZnO thin films[6]. Sodium zincate bath was prepared by using one molar zinc sulphate

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[$ZnSO_4 \cdot 7H_2O$] and 2 molar sodium hydroxide. Aluminium doping was done by adding anhydrous aluminium chloride [$AlCl_3$] in sodium zincate bath. Similarly iodine doping was done by adding iodine in sodium zincate bath. The doping concentration of both was 6 atomic %. Before deposition, the glass substrates were cleaned in chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for 10 s followed by immersion in hot water for an equal duration and the process was repeated 100 times. These samples were annealed at 450 ºC for 0.5 h in air. The structural analysis of the thin films was done by X-ray diffraction. X-ray diffraction was performed on Bruker AXS-8 using CuK_α radiation. Chemical elemental stoichiometry was examined based on energy dispersive X-ray analysis The electrical resistance of ZnO thin film at room temperature was measured by Keithley 2100 Digital Multimeter. The optical absorbance was measured in the wavelength range of 190-1100 nm by means of a UV-visible spectrophotometer. Textured grain growth of the samples was measured by using an orientation index (O.I.), which is the ratio of the intensities of (002) reflection ($2\theta = 34º$) to (101) reflection ($2\theta = 36º$) in the XRD.

$$O.I = I_{002}/I_{101}$$

RESULTS AND DISCUSSION

Structural characterization and morphological studies: XRD patterns of ZnO thin films are depicted in Figs. 1(a-b). It is seen from figures that the (002) peak appears with maximum intensity at $2\theta = 34º$. The other peaks at 31º and 36º can be associated with (100), (101) reflections of ZnO, as is expected for wurtzite hexagonal structure (JCPDS No. 36-1451). Table-1 gives the orientation index, resistance, band gap of pure, Al-doped and I-doped samples.

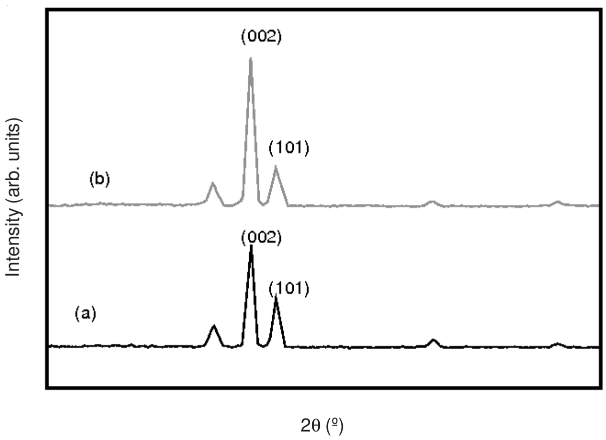

Fig. 1. XRD patterns of the samples doped with (a) aluminium (b) iodine

TABLE-1
ORIENTATION INDEX, RESISTANCE, BAND GAP OF PURE, Al-DOPED AND I-DOPED SAMPLES

Sample No.	Sample details	Orientation index (O.I.)	Resistance in MΩ at room temp.	Band gap in eV
1	Undoped sample	1.21	7.11	3.30
2	Al-doped	2.12	1.41	3.11
3	I-doped	4.30	3.80	3.21

It is particularly observed that the intensity of the (002) peak is enhanced with aluminium and iodine doping. The (002) diffraction peak exhibited a higher intensity, indicating that the grain growth is along (002) plane. Also increase in orientation index indicates the increases in the crystallinity in ZnO thin films.

Resistance measurements: The thin film resistivity greatly influenced by the interaction of the conduction electrons with the surface. In other words, it is a measure of the material's inherent surface resistance to current flow. From Table-1 it is clear that the electrical resistance in aluminium and iodine doped samples are much less than that of undoped sample.

Optical properties of ZnO films: Fig. 2 shows the optical absorbance spectrum of Al-doped ZnO thin film using UV-visible region from 200-800 nm. The Fig. 2 (inset) depicts the plot of $(\alpha h\nu)^2$ *vs.* energy, hν. The corresponding optical band gap of the sample is estimated by extrapolation of the linear relationship between $(\alpha h\nu)^2$ and hν, according to the equation $h\nu = A\ (h\nu - E_g)^{1/2}$, where α is the absorption coefficient, hν is the photon energy, E_g is the optical band gap and A is a constant. The values of direct band gap (E_g) are calculated from the intercept of $(\alpha h\nu)^2$ *vs.* hν curve. The presence of a single slope in the plot suggests that the film has direct and allowed transition. The band gap value of Al-doped ZnO thin film is found to be 3.11 eV which is slightly smaller than the reported value (3.37 eV). This difference is due to the fact that the values of band gap E_g depend on many factors like the granular structure, the nature and concentration of precursors, the structural defects and the crystal structure of the films, *etc*. Moreover, departures from stoichiometry, form lattice defects and impurity states. It is also reported that the band gap difference between the thin films is due to the grain boundaries and imperfections of the polycrystalline thin films[17]. The Fig. 3 shows the optical absorbance spectrum of I-doped ZnO thin film and Fig. 3 (inset) depicts the plot of $(\alpha h\nu)^2$ *vs.* energy. Table-1 and Fig. 4 show that band gap increases with increase in resistance of the film.

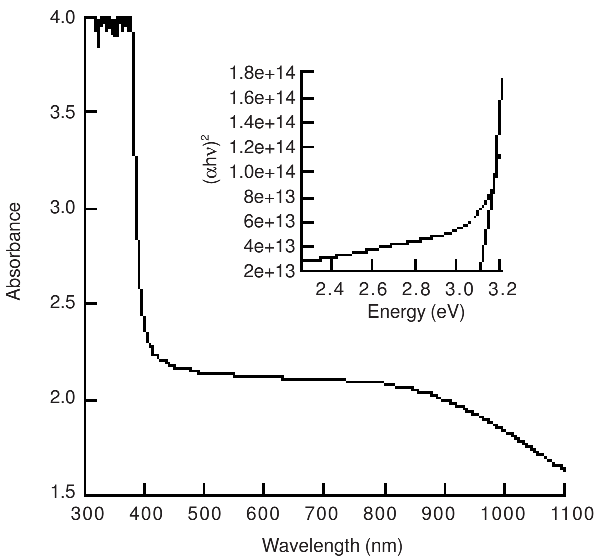

Fig. 2. Absorbance for the sample doped with aluminium. The inset indicates optical band gap energy of the sample

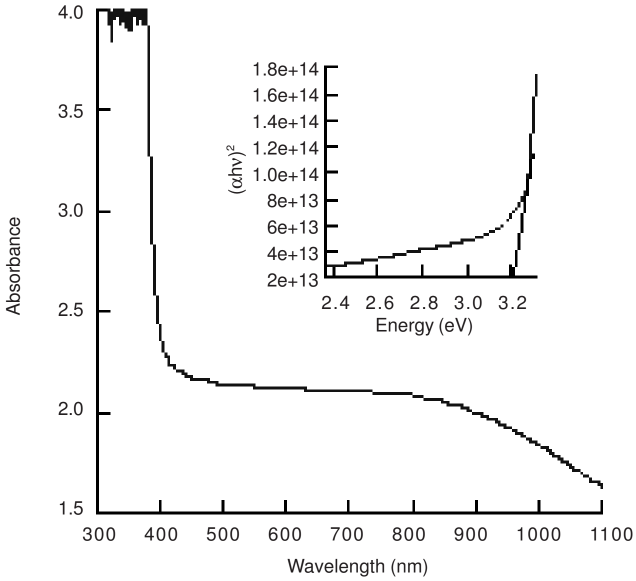

Fig. 3. Absorbance for the sample doped with iodine. The inset indicates optical band gap energy of the sample

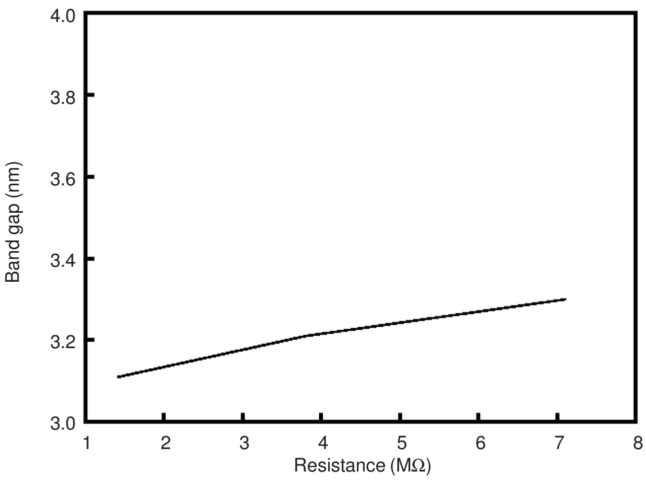

Fig. 4. Plot of band gap *vs.* resistance of different samples

Elemental analysis by EDAX: Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. From the EDAX data it is found that atomic percentage of oxygen in undoped sample is 27.34 % whereas in Al- and I-doped samples are 25.02 and 23.45 %, respectively. This means that atomic percentage of oxygen are less in Al- and I-doped samples compared to undoped samples.

Mechanism behind the oriented grain growth: Native or intrinsic defects are imperfections in the crystal lattice. They include vacancies (missing atoms at regular lattice positions), interstitials (extra atoms occupying interstices in the lattice)[18]. The iodine have more electron than oxygen and when it is inserted in oxygen site it results in defects. It is reported that Al-doping will create defects due to the substitution of Zn by Al[6]. These defects are responsible for the enhanced textured grain growth. EDAX data supports this.

Conclusion

From the studies following conclusions were drawn. Textured grain growth in ZnO thin films is enhanced by aluminium and iodine doping. When the textured grain growth increases, crystallinity of the thin film improves, resistance & band gap decreases. A possible mechanism for the oriented grain growth is also investigated. It is inferred that, the creation of defects are responsible for the enhanced textured grain growth in ZnO thin films by aluminium and iodine doping.

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