Oriented grain growth in ZnO thin films by Iodine doping

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Abstract. ZnO thin films were prepared by Successive Ionic Layer Adsorption Reaction (SILAR) method. Oriented grain growth in Iodine doped ZnO thin films were studied. The oriented grain growth in samples was studied by comparing the peak intensities from X-ray diffraction data and surface morphology by scanning electron microscopy. It is found that oriented grain growth significantly enhanced by Iodine doping. When the oriented grain growth increases, crystallinity of the thin film improves, resistance and band gap decrease. ZnO thin films having good crystallinity with preferential (002) orientation is a prerequisite for the fabrication of devices like UV diode lasers, acousto-optic devices etc. A possible mechanism for the oriented grain growth is also investigated. It is inferred that creation of point defects is responsible for the enhanced oriented grain growth in ZnO thin films when doped with iodine.

Key words: ZnO thin film, SILAR method, oriented grain growth, annealing ZnO thin films, Iodine doping.

1. Introduction

For nearly half a century, the synthesis and characterization of ZnO thin film is an active area of research. ZnO with wurtzite structure [1] is an n-type semiconductor with direct band gap of 3.37eV [2] and high electronic mobility. As a wide and direct band gap semiconductor, nanostructured ZnO thin films have attracted more attention in optoelectronic devices [2]. Different methods have been applied to obtain ZnO thin films. These include magnetron sputtering [3], chemical bath deposition [4], sol-gel [5], spray pyrolysis [6] etc. Chemical deposition techniques are relatively low cost processes and can be easily scaled up for industrial application. Among the thin films deposition methods, double dip technique from aqueous solutions is the simplest and the most economical one. There are reports that oriented grain growth (textured grain growth along c-axis) in ZnO thin films is enhanced by doping. Controllable n-type doping is easily achieved by substituting Zn with group-III elements like Al [7, 8] or substituting oxygen with group-VII elements such as iodine . There are reports on enhancement of oriented grain growth in ZnO by Al doping. But a study on the effect of Iodine doping on oriented grain growth in ZnO by iodine doping and its possible mechanism is not yet reported.

2. Experimental

ZnO thin films were prepared by Successive Ionic Layer Adsorption Reaction (SILAR) method. In which, the ZnO thin film was coated on the glass substrate (26 × 76 mm) by alternately dipping the substrate in sodium zincate bath at room temperature and then in hot water maintained at 90-95°C. Iodine doping was done by adding 6 atom.% iodine in Sodium Zincate bath. The pure and doped samples were annealed at 450°C for half an hour in air. The structural analyses of the thin films were done by X-ray diffraction (XRD) and surface morphology by scanning electron microscopy (SEM).

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Chemical elemental stoichiometry was examined from energy dispersive X-ray analysis (EDAX) linked with SEM unit. The resistance of ZnO thin film at room temperature is measured by Keithley 2100 Digital Multimeter. The optical absorbance was measured in the wavelength range of 190-1100 nm by means of a UV-VIS spectrophotometer. Oriented grain growth of the samples was measured by using an orientation index (O.I.), which is the ratio of the intensities of (002) reflection ($2\theta = 34^\circ$) to (101) reflection ($2\theta = 36^\circ$) in the XRD.

In the course of the present investigations, oriented grain growth in ZnO thin films doped with iodine is studied. A possible mechanism for the enhanced oriented grain growth is also investigated.

3. Results and Discussion

3.1 Structural and Morphological Studies

XRD patterns of ZnO thin films of pure and doped samples are depicted in fig1.(a-b).

It is seen from figures that the (002) peak appears with maximum intensity at $2\theta = 34^\circ$. The other peaks at $31^\circ$ & $36^\circ$ can be associated with (100), (101) reflections of ZnO, as expected for wurtzite hexagonal ZnO structure (JCPDS no.36-1-1451). In particular, it is clearly observed that the intensity of the (002) peak enhanced by doping with iodine. The (002) diffraction peak exhibited a higher intensity, showing a fact that the oriented grain growth is along (002) direction. The figure-2 shows the SEM micrograph of the iodine doped sample. The flowered structure of ZnO is evident from the SEM micrograph.
The average grain size of the ZnO crystals in the films was calculated by using Scherrer’s formula: \( D = \frac{0.9\lambda}{\beta \cos \theta} \), where \( D \) is the grain size, \( \lambda \) the wavelength of X-ray used, \( \beta \) the FWHM (Full width half maximum) and \( \theta \) Bragg diffraction angle of the XRD peak. From the studies, the grain size of the iodine-doped sample was found to be 35.05nm (Table-1). The dislocation density \( \delta = \frac{1}{D^2} \) where \( D \) is the grain size. Dislocation density gives the degree of crystallinity. The larger values of \( D \) indicate better crystallization of the films. As the values of \( D \) increase, the orientation index is found to increase. Increase in orientation index indicates the increase in the crystallinity of ZnO thin films. ZnO thin film having good crystallinity with preferential (002) orientation is a prerequisite for the fabrication of devices like UV diode lasers [2].

3.2 Resistance Measurements

The grain size and resistance of ZnO thin films measured at room temperature is given in table-1. It shows that as the grain size increases, the resistances of the film decreases. One of the reasons for this is due to the decrease in grain boundary when the grain sizes increase. Another is due to the contribution of iodine ions on the substitutional site of oxygen ions.

| Sample No. | Sample details | O.I. | Grain size (D) in manometer | Resistance in K\(\Omega\) at room temp. | Band gap in eV |
|------------|----------------|-----|----------------------------|----------------------------------------|---------------|
| 1          | Pure           | 1.21| 18                         | 9.01                                   | 3.25          |
| 2          | Iodine doped   | 7.1 | 35.05                      | 3.51                                   | 3.12          |

3.3 Optical Properties of ZnO Films

Fig.3 shows the optical absorbance spectrum of the pure ZnO thin film using UV-visible region from 200-800nm. The corresponding optical band gap of the thin film is estimated by extrapolation of the
linear relationship between \((\alpha \nu)^2\) and \(\nu\) according to the equation: \(\nu = A (\nu - E_g)^{1/2}\) where \(\alpha\) is the absorption coefficient, \(\nu\) is the photon energy, \(E_g\) is the optical band gap and \(A\) is a constant.

The presence of a single slope in the plot suggests that the film has direct and allowed transition. The band gap of the pure sample is found to be 3.25 eV which is slightly smaller than that of bulk ZnO (3.37 eV). 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 [9]. The corresponding band gap of iodine doped sample is reported in the table-1. The table-1 shows that band gap decreases with increase in grain size of the film.

3.4 Mechanism

From EDAX analysis it is observed that the atom. % of oxygen in pure and doped samples 27.34% and 30.97 whereas Zn is 72.66 and 69.03 respectively.

Native or intrinsic defects are imperfections in the crystal lattice that involve only the constituent elements. They include vacancies (missing atoms at regular lattice positions), interstitials (extra atoms occupying interstices in the lattice) and anti sites (a Zn atom occupying an O lattice site or vice versa) [10]. Iodine has one more electron than oxygen and when inserted on the oxygen site, it acts a shallow donor in ZnO. Therefore, the atom. % of Zn is low compared to pure sample. From this it is clear that the creation of point defect is the mechanism behind the oriented grain growth.

4. Conclusion

Oriented grain growth in ZnO thin film is enhanced by iodine doping. When the oriented grain growth increases, crystallinity of the thin film improves, resistance and band gap decrease. ZnO thin film having good crystallinity with preferential (002) orientation is a prerequisite for the fabrication of devices like UV diode lasers, acousto-optic devices etc. A possible mechanism for the oriented grain growth was also investigated. It is inferred that creation of point defects is responsible for the enhanced oriented grain growth in ZnO thin film by iodine doping.

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