

Effect of annealing on structural, electrical and optical properties of pure and doped ZnO thin films under different oxygen partial pressures

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Introduction

For nearly half a century, the synthesis and characterization of ZnO thin films has been an active area of research. ZnO with wurtzite structure is an n-type semiconductor with direct band gap of 3.37eV and high electronic mobility. As a wide and direct band gap semiconductor, nanostructure ZnO thin films have attracted more attention in optoelectronic devices [1-4]. The transparent conductive oxide (TCO) electrodes using Al-doped ZnO have attracted much attention as a powerful candidate material for ITO transparent electrodes. 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. Different methods have been applied to obtain ZnO thin films. These include magnetron sputtering, chemical bath deposition, sol-gel, spray pyrolysis etc. Chemical deposition techniques are relatively low cost processes and can be easily scaled up for industrial application [5]. 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 [6], (Successive Immersion Layer Adsorption Reaction) 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 desirable for applications such as UV diode lasers, acousto-optic devices etc. There are reports of enhanced textured grain growth in ZnO thin films by doping and annealing. Moreover, the band gap of the material can be tuned from 3.37 to 3.2 eV if it is doped with group III metal ions.

In course of the present investigations, nano- structured ZnO thin films were prepared by Successive Ionic Layer Adsorption Reaction (SILAR) method. Doping of ZnO with Aluminium, Iodine, tin and cadmium were done. The samples were annealed under different oxygen partial pressures by annealing the samples in Air, Oxygen, Nitrogen and Argon atmospheres. The effect of doping and annealing on structural, electrical and optical properties of ZnO thin films have been studied.

Experimental

ZnO thin films were prepared by 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 . Sodium Zincate bath was prepared by using 1M Zinc Sulphate [ZnSO₄ .7H₂O] and 2M Sodium hydroxide [NaOH]. Aluminium doping was done by adding anhydrous Aluminium Chloride [AlCl₃] in Sodium Zincate bath. The doping concentration was 6 atm%. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for 10sec followed by immersion in hot water for the same time and it was repeated for 100 times. The undoped and doped samples were annealed at 450° C for half an hour in air, oxygen, nitrogen and argon atmospheres. The flow rate of the gases was 2 liters/minute. The structural analysis of the thin films was done by X-ray diffraction (XRD) and surface morphology by scanning electron microscopy (SEM). X-ray diffraction was performed on Bruker AXS-8 using CuK α radiation and SEM photographs were taken by using JEOL -JSM6490. 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 was measured by Keithley 2100 6 1/2 Digital Multimeter.

Results and Discussion

Optimization of the synthesis parameters of ZnO thin film on glass substrate by SILAR (double dip) method

Successive Ion Layer Adsorption and Reaction (SILAR) technique was used for the preparation of nano ZnO thin films. ZnO thin films were deposited on glass substrate by alternate dipping of the substrate in sodium zincate bath at room temperature and hot water maintained nearly at boiling point. The parameters such as concentration, temperature and dipping time etc. for the synthesise of phase pure ZnO thin films were optimized. The chemical reaction for the formation of ZnO is

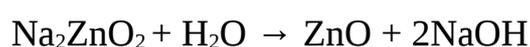


Fig.1 shows the XRD pattern of the pure sample

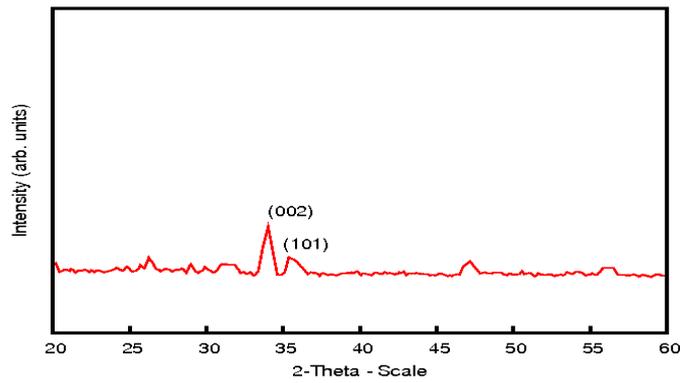


Fig 1

The d- values and corresponding intensities of the prepared samples are in agreement with the standard values of ZnO. The values are shown in table 1

Standard values			Observed values		
2 θ	d value (Å)	Relative Intensity	2 θ	d value (Å)	Relative Intensity
31.737	2.81716	56.9	31.737	2.81716	56.9
34.379	2.61582	41.5	34.379	2.61582	41.5
36.215	2.47843	100	36.215	2.47843	100
47.484	1.91322	21.2	47.484	1.91322	21.2

Table -1

SEM photograph of the sample is shown in fig.2

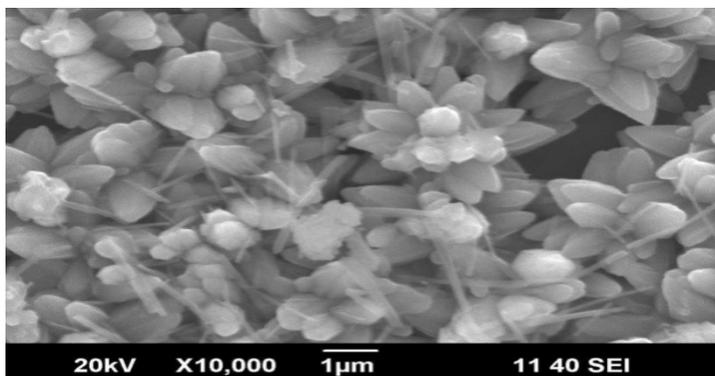


Fig.2

From the SEM photograph of pure sample, it is clear that prepared samples have needle and flower like structure.

Doping of ZnO thin films with metal ions

The ZnO thin films were doped with different elements like Al, I, Sn & Cd . One of the important observations is that, doping ZnO with Aluminium, Iodine and Tin gives textured grain growth along (00l) planes. The 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 ($2\theta = 34^\circ$) to (101) reflection ($2\theta = 36^\circ$) in the XRD.

$$\text{i.e, O.I.} = I_{002}/I_{101}$$

The above mentioned reflections are shown in fig.3

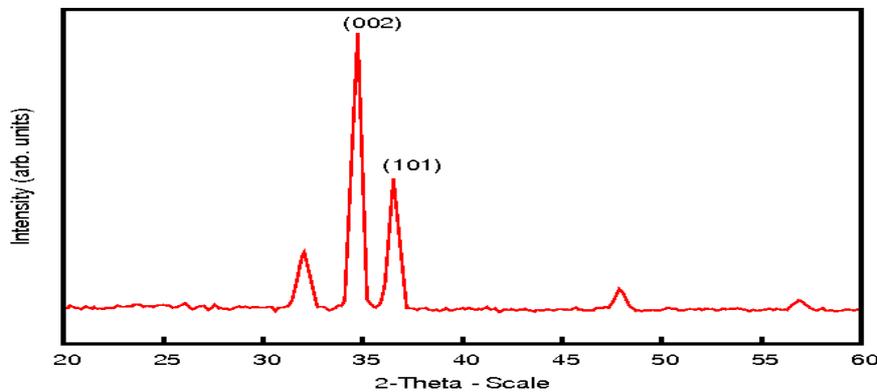


Fig 3

The band gap of the samples were determined from the UV spectrum. Fig.4 shows UV spectrum of pure sample and the inset indicates optical band gap energy of the sample.

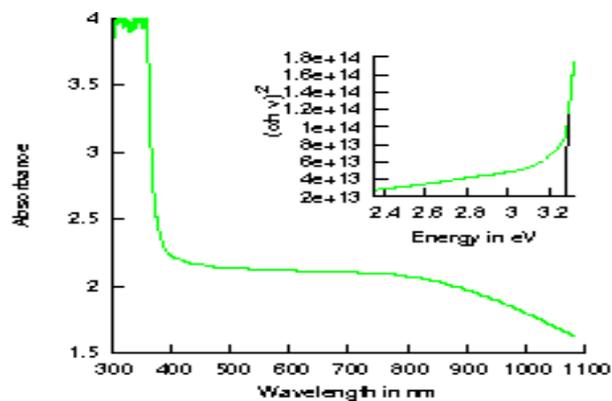


Fig. 4

The orientation index, resistance and band gap of the samples are given in table-2

Sample details	Orientation index	Resistance $K\Omega$	Band gap eV
Pure	1.21	7.11	3.3
Al- doped	2.12	1.41	3.11
I- doped	4.3	3.8	3.21
Sn- doped	4.61	2.25	3.11
Cd- doped	1.23	3.01	3.19

Table -2

From the table it is clear that O.I. of Al, Sn & I doped samples are found to be increased and maximum in the case of Sn doped samples. But in the case of Cd doping there is no textured grain growth. And it is also evident from the table that while doping the band gap and resistance of the samples is decreasing.

The fig.5 shows the SEM photographs of the pure and Al-doped samples.

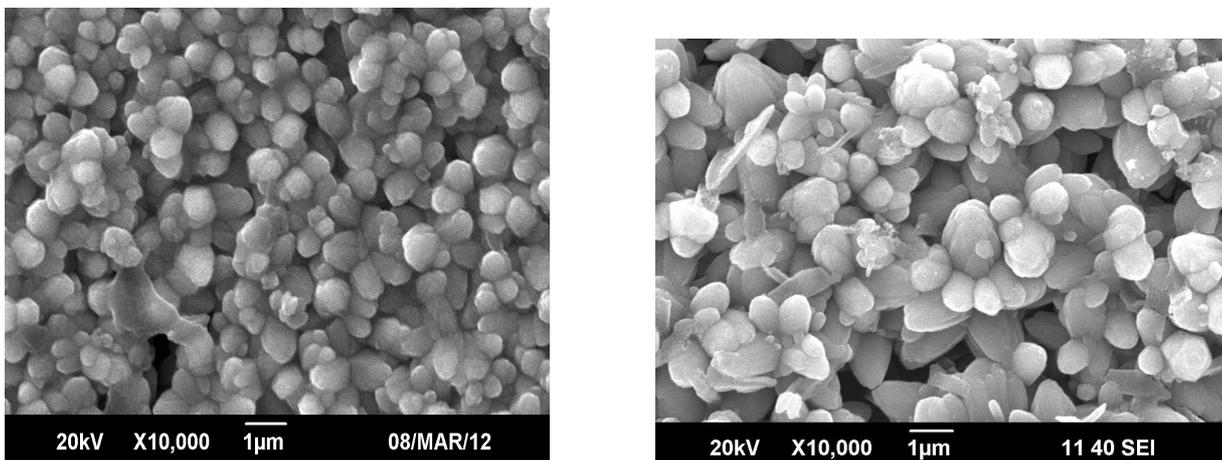


Fig.5

From fig.5 the grain growth of the Al- doped sample is clear.

The fig. 6 & 7 show the field dependent photoconductivity of pure and Cd doped ZnO thin film respectively.

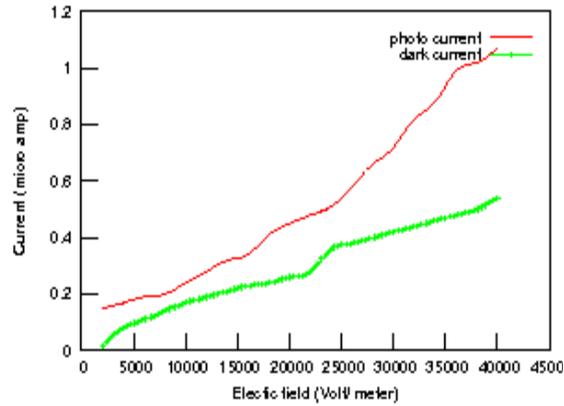


Fig 6

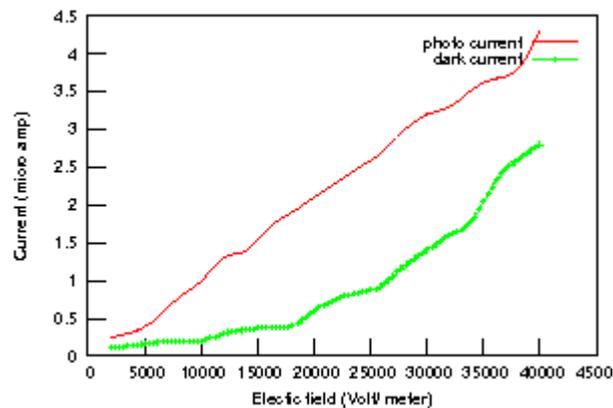


Fig 7

From the figures it is clear that, in the case of Cd- doped sample, photo current and dark current are more compared to pure sample. This makes them promising candidate for solar cells.

Effect of annealing under different oxygen partial pressures

The samples were annealed in different oxygen partial pressures ie in Oxygen atmosphere, Nitrogen atmosphere, and Argon atmosphere. The structural, electrical and optical properties of these samples were studied and corresponding values are shown in the table-3

Sample details	Orientation index	Resistance M Ω	Band gap eV
Oxygen flow rate 2.5 liters/min	2.2	4.8	3.21
Oxygen flow rate 3.5 liters/min	1.72	5.5	3.23
Oxygen flow rate 4.5 liters/min	1.31	6	3.26

Table 3

From the table, it is evident that, as the oxygen flow rate decreases, orientation index increases, resistance and band gap decreases.

Table-4 gives the orientation index, resistance and band gap of the samples annealed in air, Argon and Nitrogen atmospheres.

Sample details	Orientation index	Resistance M Ω	Band gap eV
Annealed in air	1.23	9	3.3
Annealed in argon atmosphere	1.47	6	3.21
Annealed in nitrogen atmosphere	1.7	4	3.11

Table 4

From the table it is evident that the sample annealed in Nitrogen atmosphere has more orientation index, low resistance and band gap compared to samples annealed in air and Argon atmosphere. Same result was obtained when doped samples were annealed in air, Argon and Nitrogen atmospheres.

Conclusions

From the studies following conclusions can be drawn:

1. Parameters for the synthesis of phase pure ZnO thin films by SILAR method have been standardized.
2. Doping of ZnO by Al, Sn and Cd were done. By doping with Al, I and Sn gives textured grain growth along (00l) plane. Textured grain growth is maximum in the case of Sn doped samples compared to other samples. But there is no textured grain growth by Cd- doping. And it is also found that, while doping, the band gap and resistance of the samples are decreasing. In the case of Cd doped sample, photo current and dark current is more compared to pure samples. This makes them promising candidate for solar cells.
3. Effect of annealing under different oxygen flow rates was studied. When oxygen flow rate decreases textured grain growth increases, band gap and resistance decreases.
4. Annealing of the samples in air, argon and nitrogen atmospheres were also done. The sample annealed in nitrogen atmosphere have more textured grain growth, low resistance and band gap compared to samples annealed in air and argon atmospheres. Same result was obtained when doped samples were annealed in air, argon and nitrogen atmospheres. Zinc oxide crystallites with preferential grain growth along c-axis are desirables for applications such as UV diode lasers, acousto-optic devices etc.

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List of publications

1. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Oriented grain growth in ZnO thin films annealed under Oxygen, Air and Nitrogen atmosphere and by doping*” Presented in the National Seminar on “Emerging trends in optoelectronic and solar energy materials (EOSN 2011)”, PRNSS College Mattannur, 23-24 Sep. 2011.
2. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Oriented grain growth in ZnO thin films by Iodine doping*”, Presented in the International conference on “Materials science and technology ICMST-2012”, St.Thomas College, Pala,10-14 June 2012 (IOP conference series)
3. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Studies on effect of oxygen flow rate in textured grain growth of ZnO thin films*” Presented in the International conference on “Materials science and technology ICMST-2012”, St.Thomas College, Pala,10-14 June 2012 (IOP conference series)
4. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Textured grain growth in ZnO thin films by Tin doping*” Presented in the national seminar on “*Emerging nano science and its future in biology (ENFB 2012)*”, St. Aloysius College, Edathua, 21-23 Aug. 2012.
5. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Studies on variation in textured grain growth in ZnO thin films by Aluminium and Iodine doping*” presented in the “ International conference on nano science and nano technology (ICOON 2013)”, SRM University, Chennai and published in “*Asian journal of Chemistry*” 18-20 March 2013.
6. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Variations of Textured grain growth in pure and Cd doped ZnO nano thin films*” *Journal of NanoScience and NanoTechnology* Vol 1 Issue 2 Summer Edition June 2013 Pp 59-62
7. Deepu Thomas, Sunil C. Vattappalam, Sunny Mathew and Simon Augustine “*Preparation and characterization of Li doped ZnO thin films deposited by SILAR method*” Presented in the National Seminar on “Recent Trends In conducting Polymers and Polymer Nano Structures”, Aquinas college Eda Cochi, 29-30 Aug. 2013.