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Effect of Aluminium Doping on Structural, Optical and Electrical Properties of Silar Prepared ZnO Thin Films

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Abstract: Structural, Optical and Electrical properties of ZnO and AZO (ZnO:Al) thin films were studied. Successive Ionic Layer Adsorption and Reaction (SILAR) technique was employed to prepare pure ZnO and AZO thin films, which offer advantages like: the simple and cheap tools. SILAR method for metal oxide involved a relatively great number of process parameters: pH, Bath temperature, Number of dippings. Pure and Al doped ZnO (AZO) thin films were deposited from ammonium zincate bath on microscopic glass substrates with varying dopant concentration (1, 5 and 7%). Structural characterization of the SILAR prepared samples were analysed using X-Ray diffraction (XRD) technique. Incorporation of Al was noted from elemental analysis EDX. The spherical shape of ZnO particles were confirmed by SEM micrograph. Band gap energy for samples was determined from UV-Visible spectroscopy. From the four probe technique, it was found that, the films exhibited resistivity changes due to the concentration of Al content. Among the many materials ZnO is the typical sensing material for gas sensing applications.
Key Words: ZnO thin films, II –VI semiconductors, Al doppings.

Introduction

ZnO as a wide band gap semiconductor occupies a special position because of its variety of striking properties such as the electrical conductivity and optical quality. ZnO thin films plays an important role in both application and performance aspects in semiconductor industries. Metal oxide semiconductors are the attractive research area because of its various technological applications such as gas sensors[1, 2], solar cells[3], surface acoustic wave devices[4], thin film transistors[5]a transparent electrode[6], piezoelectric devices[7].

ZnO is a very important II-VI semiconductor compound and has a direct band gap around 3.2-3.37eV with a high exciton binding energy 60meV. ZnO films has been doped with metal ions such as Indium (In), Gallium (Ga), Cadmium (Cd), Aluminium (Al) etc. To improve their structural, optical and electrical properties. Among various chemical and physical methods SILAR method is preferred for obtaining undoped and doped films for this present study. SILAR method is a modified chemical bath deposition technique[8]. Al is chosen as the dopant material because of its abundance and they have got potential applications in solar cells, solid-state display devices, optical coatings etc.

Experimental Details

Pure and Al doped thin films were deposited on cleaned glass substrates with different dopant concentrations (1, 5, 7 at %) by SILAR technique which involved dipping of substrate in ammonium zincate bath and hot water bath maintained near boiling point[9, 10]. The ammonium zincate bath was prepared by adding ammonium hydroxide (~25% pure ammonia solution; Merck, Mol.Wt 17.03g/mol, density 0.91) to an aqueous solution of zinc acetate dyhydrate(ZnCH$_3$COO)$_2$.H$_2$O) Al doping was achieved by adding different proportions (1,5,7 at %) of AlCl$_3$.6H$_2$O (Merck) with the precursor solution.50 dipping were performed for this experiment. Dipping time was 2seconds. The details of ZnO thin films preparation from ammonium zincate bath has been reported by modal et al[11]

Results and Discussion

The XRD patterns of undoped and Al doped thin films were recorded for different Al concentrations shown in figure 1. It is evident that from the intensity peaks that the improvement of crystallinity at 7at.% of Al concentration. The diffraction pattern reveals good crystalline quality. It is seen from figure1, the major diffraction peak appears along (002) plane at 34.321^0. Other low intensity peaks were observed along (100), (002), (101), (110) and (103) planes. These results suggest that there are no phase segregation or secondary phase formation as well as Al incorporation into ZnO lattice. The quantitative information was obtained from texture coefficient (TC) along the preferential crystal orientation plane (002) from the following formula [12]

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{\sum_n I(hkl)/I_o(hkl)} \times 100\%$$

Where I(hkl) is the measured relative intensity of a plane (hkl) and I$_0$(hkl) is the standard intensity of the plane (hkl) taken from the JCPDS data (Card No: 36-1451). The value TC(hkl) = 1 represents films with randomly oriented crystallites, while higher values indicate the abundance of grains oriented in a given (hkl) direction. The texture coefficient show increasing trend due to the addition of dopants of various concentrations (0at.%, 1at%, 5at.%, 7.at%) and the values are 1.193, 2.048, 2.313, 2.924 respectively. this kind of result has been explained by mondal et al[11]

The grain size of the film from the XRD data was calculated using the Debye –Scherrer formula.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where k=0.94 is the shaping factor, λ is the x-ray wavelength of CuK$_\alpha$ radiation, θ is the bragg's angle and θ is the full width half maximum of the peak. Crystallite size for ZnO films is reduced while adding dopants. The average crystallite size decreases from 33nm to 29nm as shown in table 1.

Table 1: Crystallite size of undoped and Al doped thin films

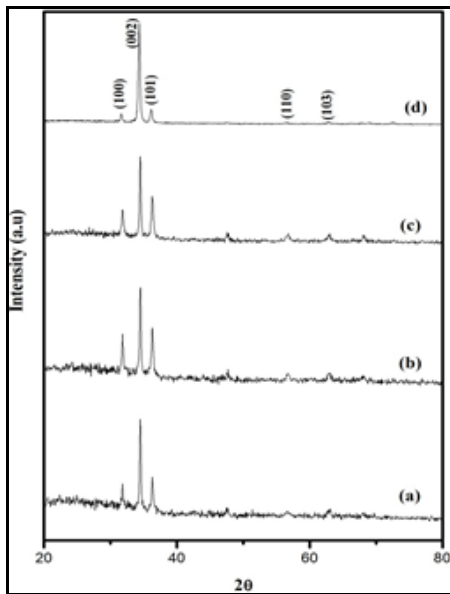| Dopant concentration	Average crystallite size
0at%	33
1at%	31
5at%	30
7at%	29

Fig 1: X-Ray Diffraction patterns of (a) undoped, (b) 1at.% (c) 5at.% and (d) 7at.% of Al doped ZnO thin film.
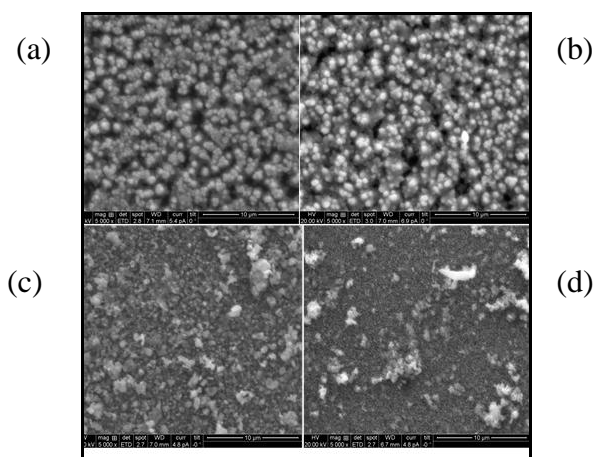

Fig 2: SEM images of (a) undoped, (b) 1at.% (c) 5at.% and (d) 7at.% of Al doped ZnO thin films

Surface morphological analysis for undoped and Al doped thin films were carried out using Scanning Electron Microscope (SEM). Figure 2 a-d show SEM images of an undoped and Al doped films. From the figure 2 it is observed that due to the incorporation of Al films looking more dense and uniform than undoped films. Distribution of Al grains led to interconnected grains and exhibit a more uniform and continuous film [12, 13].
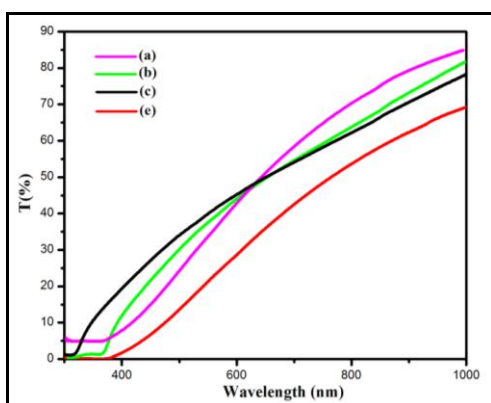

Fig 3: Transmittance spectra of (a) undoped, (b) 1at.% (c) 5at.% and (d) 7at.% of Al doped ZnO thin films
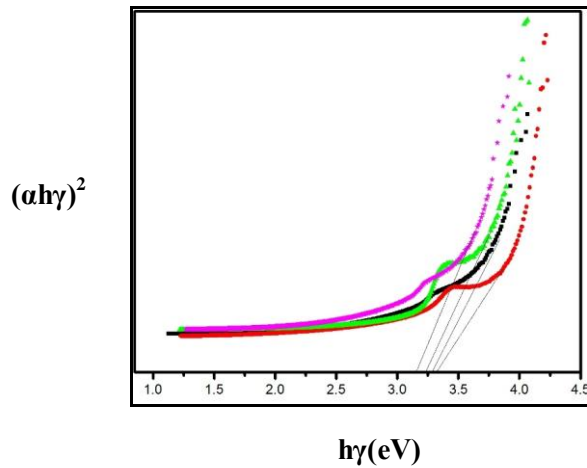
Fig 4: Optical band gap of (a) undoped, (b) 1at.% (c) 5at.% and (d) 7at.% of Al doped ZnO thin films

Optical Studies

Figure 3 shows the optical transmittance spectra of undoped and Al doped ZnO thin films as a function of wavelength range 400-1000nm. The band gaps are found to be 3.22eV for undoped sample and it is observed that band gap increases with the Al content in the ZnO films as shown in table 2. More than 80% transparency achieved for pure samples. It is clearly seen that from the figure 3 transparency decreases while adding dopants. The result is in good agreement with

Previously reported data [14].

The variation of band gap for undoped and Al doped films shown in figure 4. The optical band gap of the film was estimated using Tauac's equations, the corresponding transmittance spectra of ZnO and AZO films are shown in figure 3. Following equation relates absorption coefficient (α) and incident photon energy level ($h\gamma$).

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Where A is a function of the index of refraction and hole/electron effective masses. The direct band gap is determined using this equation when linear portion of the $(\alpha h\nu)2$ against hν plot is extrapolated to intersect the energy axis at $\alpha = 0$. Plot of $(\alpha h\nu)2$ against hν for undoped and

Table2: Band gap energy

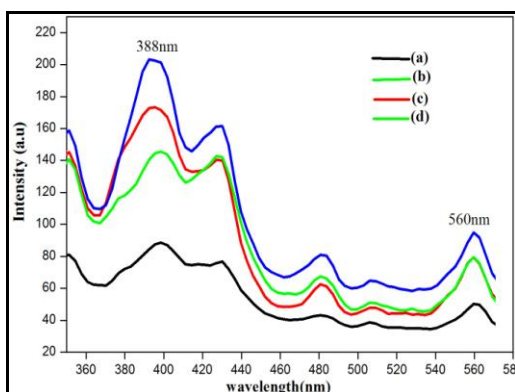| Dopant concentration in ZnO	Band gap Energy (Eg)(eV)
0at %	3.27
1at%	3.29
5at%	3.33
7at%	3.41

Fig 5: Photoluminescence spectra of (a) undoped, (b) 1at.% (c) 5at.% and (d) 7at.% of Al doped ZnO thin films

Figure 4 shows the room temperature photoluminescence spectra (PL) of SILAR prepared films. The entire samples exhibit sharp UV emission peak at 388nm and another peak at 560nm attributed to green emission in the visible region. The near band edge emission (NBE) of ZnO at 388nm is attributed to the introduction of deep level defects[15].

Electrical Studies

The variation of electrical resistivity for undoped and Al doped thin films were obtained using four point probe technique. The resistivity varies from 600kΩ to 6MΩ. The resistivity gradually increases with increasing Al concentration. Mismatch of in the ionic radii of Zn^{2+} (0.074nm) and Al^{3+} (0.054nm) may lead to the increase in resistivity of the film. Degradation of native defects such as interstitial Zn^{2+} ions and oxygen vacancies may be responsible for increase in resistivity[15].

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