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# STRUCTURAL, MORPHOLOGICAL AND OPTICAL STUDIES OF MOLARITY BASED ZnO THIN FILMS

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ZnO thin films were prepared by simple and cost effective Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Zinc sulphate and sodium hydroxide solution were used as a source of the formation of ZnO thin films. The structural, morphological and optical properties of the ZnO films were studied. Structural hexagonal wurtzite structure ZnO thin films were identified by X-ray diffraction with preferential orientation along (002) plane. The average grain size of the film is calculated using Scherer's relation and it is in the order of nanometers. The surface morphological studies of the films were analyzed by scanning electron microscope. The optical properties of the films were studied by measuring their optical transmittance as a function of wavelength. UV-VIS spectrum of the film showed that the optical band gap decreases with increase in the molarities of precursor solution.

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*Keywords*: SILAR technique, ZnO, XRD, Zinc oxide, Thin films, Optical properties, Structural and morphological studies,

## 1. Introduction

Recently zinc oxide (ZnO) has attracted much attention within the scientific community as a future material. The renewed interest in this material has arisen out of the development of growth technologies for the fabrication of high quality simple crystals and epitaxial layers, allowing for the realization of ZnO based electronic and optoelectronic devices. The electronic band structure of ZnO has been calculated by a number of groups [1-7]. The important properties of ZnO are due to its wide direct band gap of 3.37 eV [8, 9]. Bulk ZnO is quite expensive and is unavailable in large wafers. So, for the time being, thin films of ZnO are relatively a good choice. Usually, the doped ZnO films with optimum properties i.e. perfect crystallite structure; good conducting properties, high transparency and high intensity of luminescence are obtained when they are grown on heated substrates and annealed after deposition at high temperature in an atmosphere of oxygen. However, for an extensive use in the commercial applications, pure ZnO films must be prepared at much lower substrate temperatures.

In past years, many workers have investigated thin film fabrication processes for ZnO, including Sol-gel technique, Chemical bath deposition, electrochemical deposition, sputter deposition, chemical vapour deposition, evaporation, pulsed laser ablation, solid state reaction, sprays pyrolysis and SILAR technique [10-21]. Among these techniques SILAR (Successive Ionic Layer Adsorption and Reaction) is a relative new and less investigated process. As a method of thin film growth, SILAR is simple, flexible and offers an easy way to dope film. The molarity changes of precursor solution have been observed to a very critical process controlling parameter that determines the phase formation, particle size and morphology of the final film. In this work,

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the effect of molarity on the microstructure, surface morphology and optical properties of ZnO transparent films prepared by SILAR deposition method is investigated.

## 2. Experimental

The details of ZnO film deposition on glass substrate by alternate dipping into sodium zincate bath ($Na_2ZnO_2$) kept at room temperature and hot water maintained at boiling point were reported earlier [22-26]. ZnO thin films are prepared from solution in aqueous media with different molar concentration such as 0.025, 0.05, 0.075, 0.1 and 0.125 M of zinc sulphate ($ZnSO_4.7H_2O$). Zinc Sulphate was used as source of zinc and an aqueous sodium hydroxide solution was added without stirring and formed to be sodium zincate. The pH of as-prepared solution was estimated to be 9.0 ± 0.2. The cleaned substrate was immersed first in the sodium zincate and then in hot water. This cycle was repeated several times in order to increase the overall film thickness of ZnO. At various experimental conditions, was made attempt to study the effect of concentration of zinc sulphate. The prepared ZnO films were found to adhere strongly to the glass substrate. They appeared white in colour and were extremely stable under typical environmental condition. The deposited film was subsequently annealed in air at 200°C for 30 minutes. The effect of molarity was studied using various characterizations and the optimized deposition parameters are arrived for ZnO thin films.

The thickness of the samples was measured using weight-gain method uniformly for 100 numbers of dipping and it was estimated to be 0.39 μm to 1.27 μm. It is observed that the greater thickness could be grown with water as solvent at a pH of 9.0 ± 0.2 with 0.125 M (molar) concentration. With higher concentration of the zinc salts, the thickness building is quite rapid and the films begin to peel off. With lower concentration the film formation is very thin and unsuitable for structural characterization. To determine the micro structural detail of the film using X-ray diffraction using X'pert PRO (PANalytical) diffractometer with CuKα radiation and employing a scanning rate of 5° $min^{-1}$. The grain size and surface morphology of the films was determined by using scanning electron microscope (SEM) Hitachi S-3000H model. For SEM studies, the samples are precoated with Au sputtering using fine coat ion sputter JFC-1100 model instrument. Optical studies were determined by a computer controlled Perkin Elmer Lambda 35 UV-VIS spectrometer.

## 3. Results and discussion

### 3.1. XRD results

Figure 1(a) shows the X-ray diffraction patterns of the ZnO films with different molarity. It can be seen from the XRD data, that all samples are polycrystalline in nature and exhibit single phase ZnO hexagonal wurtzite structure [27] (P63mc space group, JCPDS, 36-1451) with *c*-axis (002) oriented. In addition to the (002) peak, and also observed other peaks such as (100), (101), (102), (110) (103) and (112) for higher thickness sample which are corresponding in the hexagonal ZnO phase. The intensity of (002) plane increased as the molarity of zinc sulphate is increased. The *c*-axis orientation was also reported for ZnO films deposited on oxide glass substrates by CVD [23, 24], spray pyrolysis [28]. Therefore, the *c*-axis orientation may be a common phenomenon in the ZnO film deposition by the chemical process using organo-zinc compounds. The mean crystallite size in the films were calculated using the Debye Scherrer's equation,

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

Where D is the grain size, θ is the diffraction angle, K is the shape factor (0.89), λ is the wavelength of x-ray and β is full width and half maximum (FWHM) of intense peak and also the lattice constants calculated from the most prominent peaks using equation,

$$1/d^2 = (4/3)\,[h^2+hk+k^2/a^2] + (l^2/c^2)$$

Where *h, k, l* represent the lattice planes and'd' the interplanar distance and are given in Table 1. The lattice constants calculated are found to be in good agreement with standard JCPDS data for ZnO powder. For the films grown from concentrations 0.025 M to 0.125 M, the peak position shifted to lower angles indicating increase of d value and hence the bond length. However the peak position of the principal (002) orientation is close to the JCPDS file value for the films grown from 0.1 M solutions see Figure 1(B). This may be due to the presence of large number oxygen defects. Table 1 gives the micro structural parameter values for the films grown from different molar solutions. It is clear from the results that the RMS strain, dislocation density and stacking fault probability are decreased as Zn++ concentration increased. The degree of preferred orientation I (002)/I (101) for the ZnO film prepared at 0.1 M is much higher than those others. Hence this concentration is chosen for the subsequent depositions.

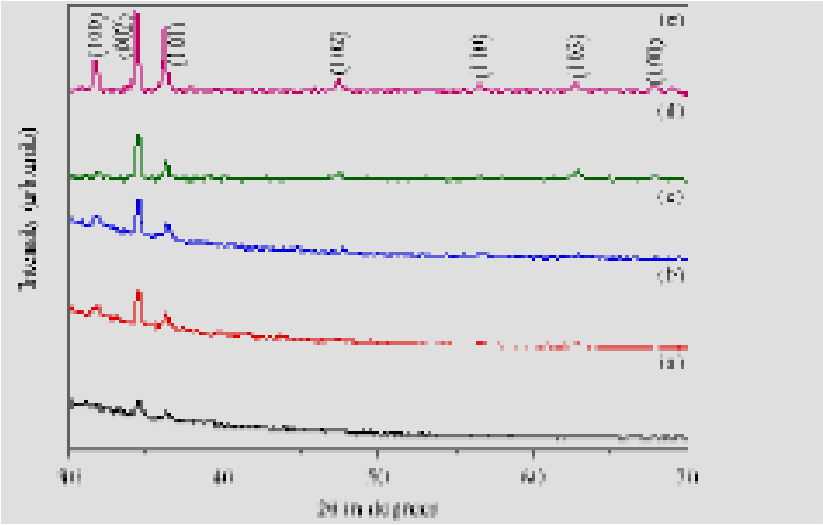

*Fig.1 (a) XRD Patterns of (a) 0.025M (b ) 0.05M (c)0.075M (d)0.1M (e)0.125M of ZnO Thin films*

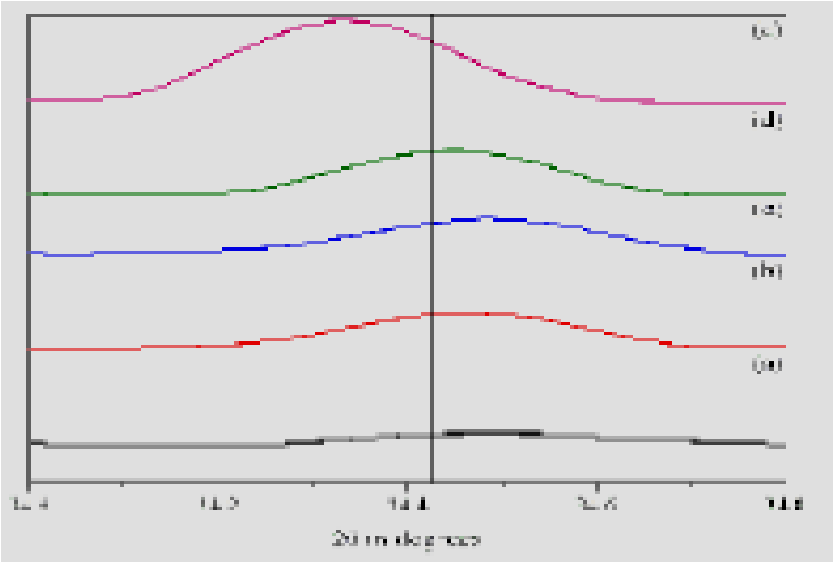

*Fig.1 (b) XRD Patterns close to (002) orientation - (a) 0.025M (b )0.05M (c)0.075M (d)0.1M (e)0.125M of ZnO Thin films*

*Table.1.Microstructural parameters of Zinc Oxide thin filmsas an effect of molarity*

| Molarity | Parameters | | | | | Lattice Constants | | $\frac{I_{002}}{I_{101}}$ |
|---|---|---|---|---|---|---|---|---|
| | t (µm) | D (nm) | $(e^2)^{1/2}$ $(10^{-4})$ | α $(10^{-4})$ | P $(10^{14})$ | a (nm) | c (nm) | |
| 0.025 | 0.39 | 26 | 49.116 | 39.214 | 6.332 | 3.285 | 5.204 | 1.23 |
| 0.05 | 0.67 | 33 | 44.834 | 36.617 | 34.784 | 3.248 | 5.205 | 1.46 |
| 0.075 | 0.91 | 47 | 41.213 | 34.819 | 32.318 | 3.234 | 5.214 | 1.51 |
| 0.1 | 1.18 | 66 | 36.712 | 32.415 | 28.315 | 3.245 | 5.207 | 2.32 |
| 0.125 | 1.27 | 87 | 30.219 | 28.834 | 24.937 | 3.271 | 5.227 | 1.24 |

### 3.2. SEM results

The SEM micrographs recorded at 20 kV with magnification 10 K are shown in Figures 2 (a-e). The average surface grain size increases with increasing molarity of the solution. The films grown at 0.025 M had spherical grains with some nano wires spread over the film surface. The films were uniform and the grains were elongated spherical grains when grown at molarity 0.05 M. The films grown at 0.075 M had hexagonal grains. Uniformly distributed hexagonal grains with good electrical contact had observed when grown at 0.1 M. At maximum molarity 0.125 M, merged hexagonal grains had been observed.

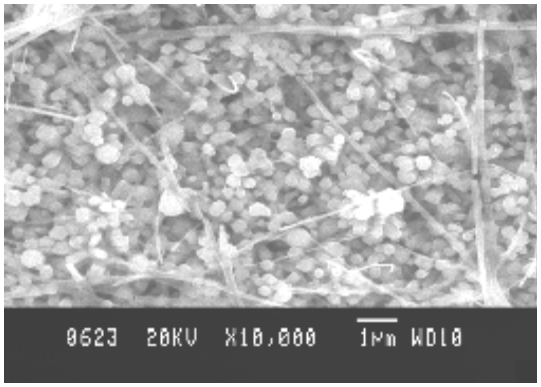


*Fig.2 (a) 0.025M of ZnO Film*

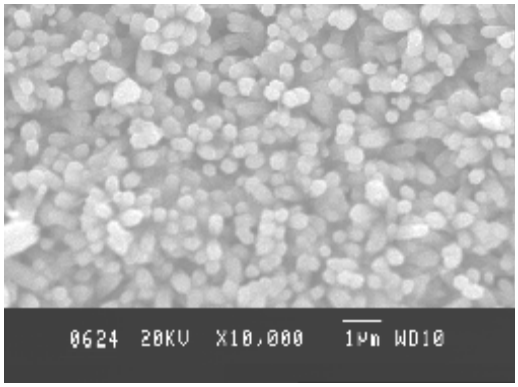


*Fig.2 (b) 0.05M of ZnO Film*

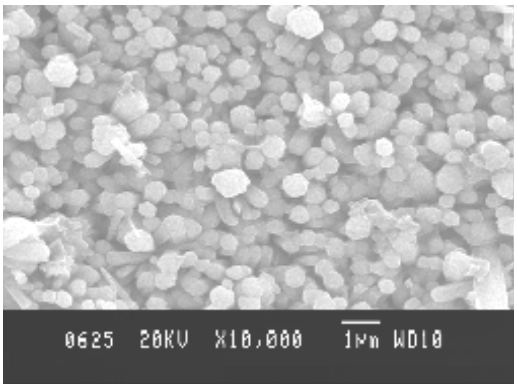


*Fig.2 (c) 0.075M of ZnO Film*

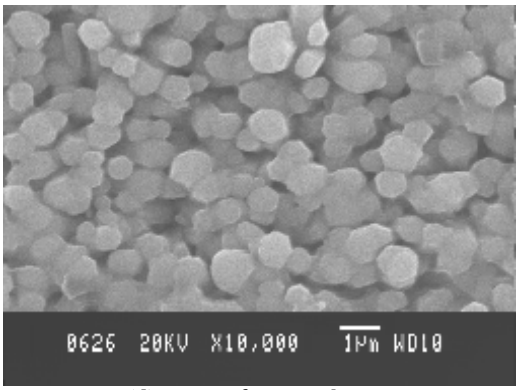


*Fig.2 (d) 0.1M of ZnO Film*

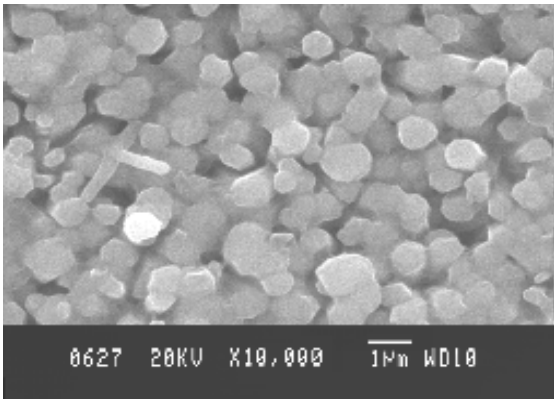


*Fig.2 (e) 0.1M of ZnO Film*

### 3.3. Optical studies

Figure 3(a) shows the optical transmittance spectra of the films in the wavelength region range from 350 to 850 nm. Transmittance over the visible range exceeds 75% for all samples. However, the film deposited from sol of molarity 0.1 has a slight decrease in transmittance. In addition, it is observed that with molarity of the precursor sol, the absorption edge in transmittance curves shows a red shift on the wavelength scale. The optical band gaps of the solution were estimated by the equation,

$$\alpha = A\,(h\nu - E_g)^{1/2}$$

Where A is a constant, $E_g$ is Energy band gap, ν is the frequency of the incident light and h is the Plank's constant. Figure 3(b) which shows a plot of $(\alpha h\nu)^2$ versus photo energy gives information about the energy of the band gap of the materials. The linear extrapolation of these curves towards the intersection with *x*-axis results in a direct band gap. These values decreased from 3.32 to 3.08 eV with increase in molarity of the precursor sol from 0.025 to 0.125 M.

These values are slightly varying than those reported in literature [29]. This may be due to our larger film thickness that might introduce strain during annealing at the interface and shift the band gap to a shorter wavelength [30, 31]. The band gap energy, a constant value of the materials for bulk samples, is known to vary in thin films due to particle size effect. It has been reported that the band gap energy can be modulated by changing the particle or grain size in the films [32]. The decrease in the optical band gap of the films with increase in the molarity of precursor solution could be attributed to the grain size enhancement.

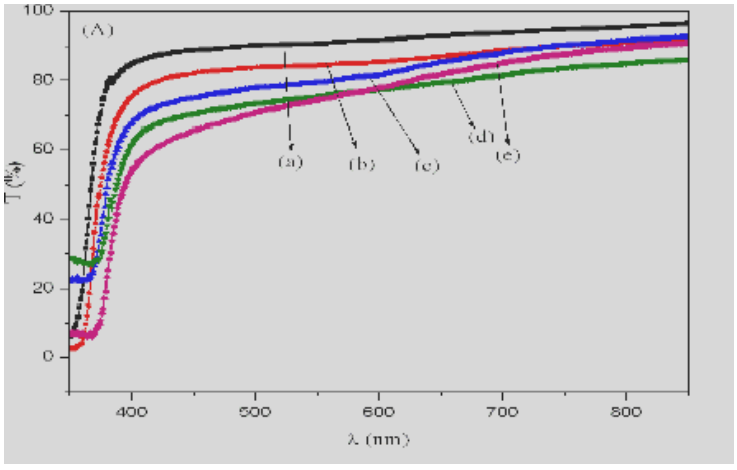


*Fig.3 (a) Optical Transmittance ccurves of (a) 0.025M (b) 0.05M (c) 0.075M (d)0.1M (e) 0.125M ZnO thin films*

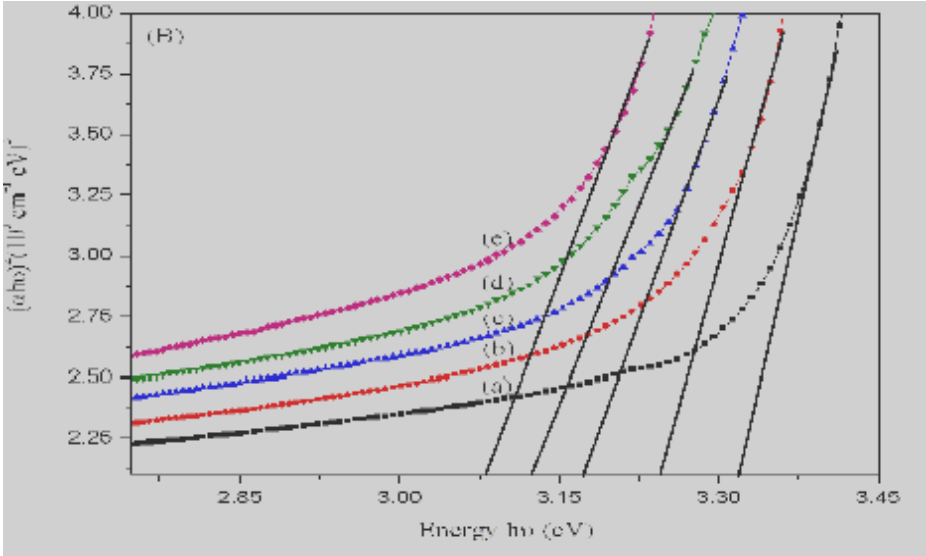


*Fig.3 (b) Optical band gap curves of (a) 0.025M (b) 0.05M (c) 0.075M (d)0.1M (e) 0.125M ZnO Thin films*

*Table 2 Optical parameters of Zinc Oxide thin films as an effect of molarity*

| **Preparation condition** | **Parameters** | **Thickness (µm)** | **Transmittance (%)** | **Band gap (eV)** |
|---|---|---|---|---|
| Molarity | 0.025M | 0.39 | 92 | 3.32 |
| | 0.050M | 0.67 | 86 | 3.24 |
| | 0.075M | 0.91 | 82 | 3.17 |
| | 0.100M | 1.18 | 77 | 3.12 |
| | 0.125M | 1.27 | 79 | 3.08 |

## 4. Conclusions

ZnO thin films were deposited by simple Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The influence of reactant concentration on the structural, optical and morphology of the film was studied. X-ray diffraction study reveals that the film has preferential orientation along the plane (002). ZnO films deposited with higher concentration of precursor solution shows clear improvement in crystallinity. All micro structural parameters of the films were calculated. The surface morphology of the films reveals that grain size depends on the molarity of the precursor solution. Transmittance over the visible range exceeds 75% for all molarity of the films. For molarity increase, the transmittance of the film decreases. The band gap of the film is situated in the range 3.32 eV - 3.08 eV and decreases with the increase of the molarity.

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