Optimization and Characterization of ZnO thin films deposited by the method of Dip Coating

S. Kalidass[a,b]

[a] Department of Electronics,
SRMV College of Arts and Science,
Coimbatore 641020, Tamil Nadu, India

[b] Department of Electronics,
Government Arts College,
Trichirapalli -620022, Tamil Nadu,India
E-mail: kalidass_rs@yahoo.com

P. Thirunavukkarasu[a,*]

[a] Department of Electronics,
SRMV College of Arts and Science,
Coimbatore 641020, Tamil Nadu, India
*Corresponding author: Ph: +91 8925556764
E-mail: iruarasu@yahoo.co.in

M. Balaji[c]

[c] Department of Physics,
Bannari Amman Institute of Technology,
Sathyamanglam, Tamil Nadu 638401, India
E-mail: balayours555@gmail.com

J. Chandrasekaran[c]

[c] Department of Physics,
SRMV College of Arts and Science,
Coimbatore 641020, Tamil Nadu, India
E-mail: jchandaravind@yahoo.com

Abstract - This effort is an illustration of the optimization of annealing temperature and mole concentration of zinc oxide (ZnO) thin films prepared by dip coating technique. The developed ZnO films were optimized and characterized by XRD, SEM, EDX, UV-Vis and I-V. The XRD analysis concludes the mole concentration and substrate temperature of the prepared ZnO films were fixed at 0.10M and 450°C, respectively. Also the XRD pattern of the optimized ZnO film reveals hexagonal structure. The SEM and EDX analysis confirmed the surface morphological variations and elemental presence. The maximum band gap value is observed as 3.03 eV for 450°C with 0.10 M from the optical properties recorded by UV-vis spectrum. The maximum conductivity value of the prepared ZnO thin film is recorded as 4.46 x 10^{-11} S/cm from I-V characterization.

Keywords – ZnO; thin films; optimization; characterization; dip coating

I. INTRODUCTION

ZnO is a very impressive material for various applications in both microelectronic and optoelectronic devices. It is a wide band gap oxide semiconductor with a direct energy gap of about 3.37 eV. As a consequence, ZnO absorbs UV radiation due to band to band transitions, while it can be used as TCO thin films, mainly for applications such as solar cells, liquid crystal displays and heat mirrors [1-4]. Furthermore, ZnO is used as semiconducting multilayer, photo thermal conversion system, gas sensors and optical position sensors [5]. Usually, ZnO crystallizes into a hexagonal wurtzite crystal structure and has a melting point of 1975°C. It exhibits a direct band gap between 3.2 and 3.45 eV and is highly conductive, which is an unusual property for wide band gap material. In ZnO, electron concentration range is observed in the range from 10^{17} - $10^{20}/cm^3$ and its mobility is around 10 - 100 cm^2/Vs resulting in a resistivity between 0.1 and 10^{-3} cm depending on conditions at the preparation. ZnO also has some very interesting optical properties. It absorbs IR light waves beyond 900 nm and transmits visible light of wavelength 400 to 700 nm. It concludes that ZnO film can be used as a TCO material in optoelectronic devices, including light emitting diodes, photo detectors, thin film solar cells, touch panels and flat panel displays.

Among all the oxide materials studied, in the last years, ZnO has emerged as one of the most promising materials, due to its optical and electrical properties, high chemical and mechanical stability, and also being abundant in nature, makes it a lower cost material when compared to the most currently used TCO materials (ITO and SnO_2). In order to improve the properties of the films, several techniques such as sputtering [6, 7], thermal evaporation [8], dip coating [9] and spray pyrolysis [10] have been applied for the production of ZnO. Dip coating technique is preferred to these other techniques because it is cheaper, simpler and more versatile than the others, as it allows the possibility of obtaining films with the required properties for different applications and also when large area of the films are needed.

In this task, investigations in relation to the dip coated ZnO thin films on glass substrates , their structural, electrical and optical characterizations are summarized. In dip coating technique, the process - parameters highly dominate the film properties. Hence, their optimization has been done to obtain high quality ZnO films with high electrical conductivity and transmittance.

II. PREPARATION CONDITIONS USED FOR ZNO THIN FILM

The solution was prepared with 0.05, 0.10 and 0.15 M of zinc acetate in 100 ml of ethanol and stirred for 45 min. Mono ethyl amine (MEA) was added into the prepared solution for ionizing and stirred for an hour. The well cleaned slide was dipped into the prepared solution and deionized water simultaneously 5 times of 30 seconds. The deionized water was kept at 85°C. After that, the prepared slides were annealed at different temperatures of 250, 350 and 450°C. So that, pinhole free and uniform ZnO films were obtained. Structural studies were carried out using the X-ray diffractometer (XRD, XPERT-PRO) with CuKα1 radiation of wavelength 1.5406 Å at a generator setting of 30 mA and 40 KV in the 2θ range from 20 to 70°. The surface morphology of the prepared thin films was investigated by the scanning electron microscope (JEOL JEM 2100). Elemental presence was confirmed by EDX (QUANTA FEG 250). The optical studies were examined by the UV-Visible spectrophotometer (Perkin Elmer Lambda 35) in the wavelength range from 300 to 900 nm. The DC electrical conductivity and diode studies of the $RuMoO_3$ films were measured by the Keithley Electrometer 6517-B.

III. RESULTS AND DISCUSSION

A. Structural Properties of ZnO Films

An XRD spectrum shows that, the concentrations of zinc acetate precursor solution were changed as 0.05, 0.10 and 0.15 M with the annealed temperatures fixed at 250, 350 and 450°C. Fig. 1 shows the XRD patterns of the films deposited at different mole concentrations of zinc acetate with different annealed temperatures. From the Fig. 1, it is seen that films are polycrystalline with hexagonal structure. X-ray diffractograms show that films were grown along (1 0 0) (0 0 2) and (1 0 1) planes, growth along (0 0 2) is dominant which is well matched with JCPDS-Card No. 89-0510. Annealing temperature is a crucial deposition parameter in dip coating technique of transparent conducting oxide films. In order to study the influence of annealing temperature on the composition and crystalline properties of ZnO films, temperatures were varied between 250 and 450˚C.

Table 1 shows the microstructural properties ZnO thin films for the preferred orientation of (0 0 2) plane. The crystallite size (D) [11], microstrain (ε), dislocation density (δ) and stacking fault (SF) values can be obtained using the following equations (1-4) [12],

$$D = \frac{k\lambda}{\beta\cos\theta} \quad ---- (1)$$

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad ---- (2)$$

$$\delta = \frac{1}{D^2}\ \text{lines/m}^2 \quad ---- (3)$$

$$SF = \left[\frac{2\pi^2}{45(3\tan\theta)^{1/2}}\right]\beta \quad ---- (4)$$

where k is the shape factor (k=0.94), λ is the wavelength of the X-ray radiation, θ is the diffraction angle and β is the full width at half maximum.

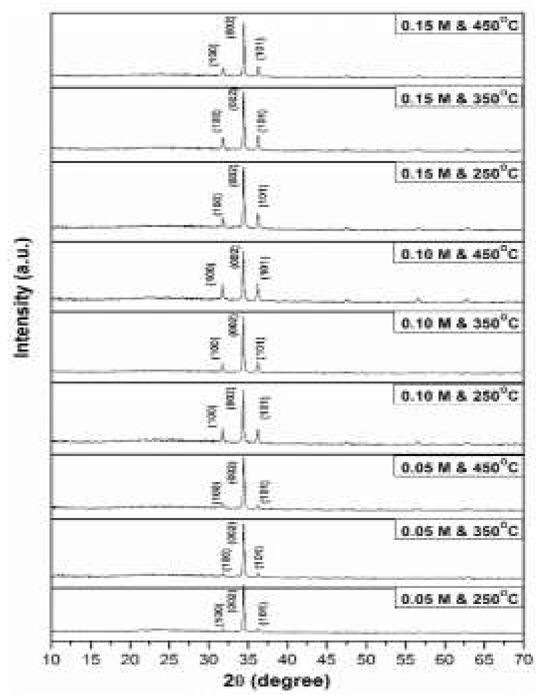

Fig. 1. The XRD pattern of ZnO thin films for different mole concentrations and annealing temperatures

Investigated ZnO films for the 2θ scans between 10˚ and 70˚ indicated a slightly (002) preferred orientation. For the films annealed between 250°C and 450°C, the increase in temperature leads to an improvement in crystallinity [13]. The film prepared at 450°C and 0.1 M exhibits a maximum crystallite size of 56.4 nm. It is evident that crystallite size of the ZnO films increases with the increase in substrate temperature for the (0 0 2) oriented crystallites for 450°C with 0.1 M. This trend of increase in crystallite size with temperature is reported already for the ZnO films [14, 15].

TABLE I THE MICTROSTRUCTURAL PARAMETERS OF ZnO THIN FILMS FOR DIFFERENT MOLE CONCENTRATIONS AND ANNEALING TEMPERATURES

Mole concentrations & annealing temperatures	Diffraction angle 2θ (deg)	Inter planar distance Å	Grain Size (D) nm	Micro strain (ε) (x 10^{-3} lines^{-2}m^{-4})	Dislocation density (x10^{14} lines/m^2)	Stacking Fault x10^{-2}
0.05 M & 250°C	34.4400	2.6041	42.3132	0.819797	5.58532	0.21598
0.05 M & 350°C	34.4513	2.6033	42.3145	0.819772	5.58498	0.21602
0.05 M & 450°C	34.4562	2.6030	42.3151	0. 819761	5.58483	0.21604
0.10 M & 250°C	34.3805	2.6085	42.3064	0. 819929	5.58712	0.21574
0.10 M & 350°C	34.3870	2.6081	42.3071	0. 819915	5.58692	0.21576
0.10 M & 450°C	34.3994	2.6071	56.4114	0.614915	3.14243	0.16186
0.15 M & 250°C	34.4369	2.6044	42.3129	0. 819804	5.58541	0.21596
0.15 M & 350°C	34.4496	2.6035	50.5315	0. 686468	3.91630	0.18089
0.15 M & 450°C	34.4712	2.6019	42.3168	0. 819728	5.58438	0.21610

The crystal defect parameters such as micro strain and dislocation density are estimated and their variations with respect to the annealed temperatures and mole concentrations are explicit from the table 1.

The minimum micro strain value is observed for 450°C with 0.1 M. This type of change in strain may be due to the recrystallization process observed in the polycrystalline oxide films. At annealing temperature 450°C with 0.1 M, micro strain, dislocation density and stacking fault are minimum as shown in table 1, which revealed the reduction in the concentration of lattice imperfections leading to highly crystallized films with preferred orientations.

B. Surface Morphology of ZnO Films

ZnO films have been prepared by dip coating technique using the optimized deposition condition of annealed temperature at 450˚C with different mole concentrations of 0.05, 0.10 and 0.15 M. The surface morphology of the dip coated ZnO films are presented in Fig. 2.

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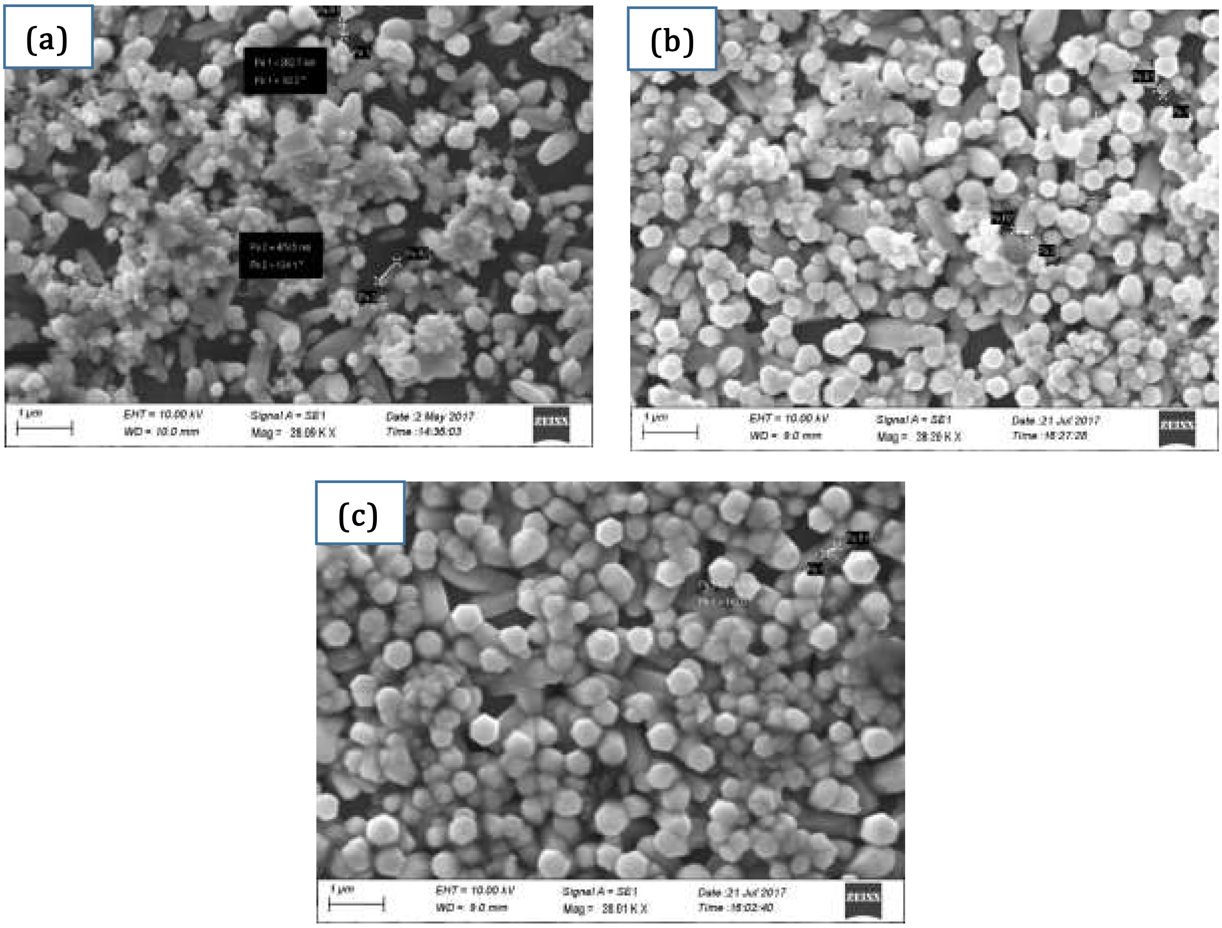

Fig. 2. The SEM images of ZnO thin films for different mole concentrations of (a) 0.05, (b) 0.10 and (c) 0.15 M at annealing temperature of 450°C

All films deposited at 450°C attain a microstructure and had a close-packed morphology. The film prepared at T_s = 450°C with 0.05 M consists of randomly oriented rice-like grains in sub-microsized size as shown in Fig. 2(a). ZnO films for 0.10 and 0.15 M show that randomly oriented benzene ring shaped microsized rods are attained (Fig. 2(b&c)). The enhancement of crystallinity at substrate temperature 450°C could be due to a large grain size therefore a better crystallinity [15].

C. Elemental Analysis of ZnO Film by EDAX

The stoichiometry analysis of the elements present in the ZnO thin film was carried out by EDAX results. Fig. 3 shows the EDAX pattern of the ZnO film deposited under the optimized conditions at annealed temperature of 450°C with the mole concentration of 0.10 M.

EDAX spectrum shows that the prepared ZnO has nearly the stoichiometric ratio of Zn and O but with some oxygen deficiency. The compositional analysis of the film prepared at the annealed temperature of

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450°C with 0.10 M indicates that the atomic percentage ratio of Zn:O as 55.10:44.90.

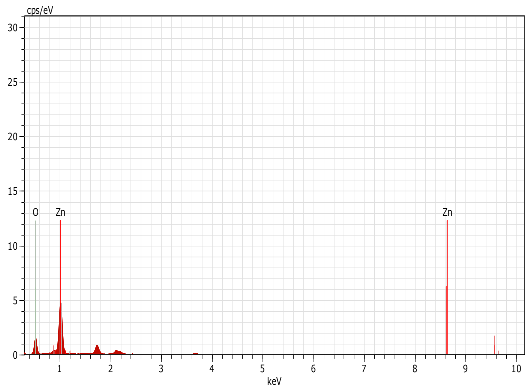

Fig. 3. The EDX spectrum of ZnO thin films for 0.10 M with annealing temperature of 450°C

D. Optical Properties of ZnO Films

Fig. 4 shows the transmission spectra with the wavelength region of 300 - 900 nm for the ZnO films deposited at different mole concentrations of 0.05, 0.10 and 0.15 M at different annealed temperatures of 250, 350 and 450°C. The maximum transmittance is around 70% at 650 nm for 0.10 M with 450°C annealed ZnO film. However, the transmission value decreases steeply in the UV region to less than 400 nm. The average percentage transmission for all the ZnO films is in the recorded wavelength region of 300 - 900 nm.

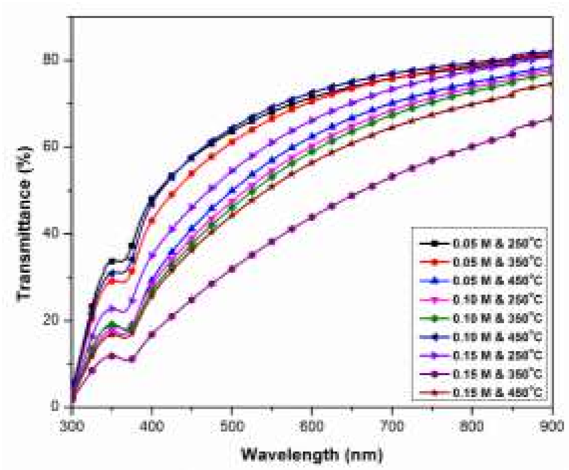

Fig. 4. The transmittance spectra of ZnO thin films for different mole concentrations and annealing temperatures

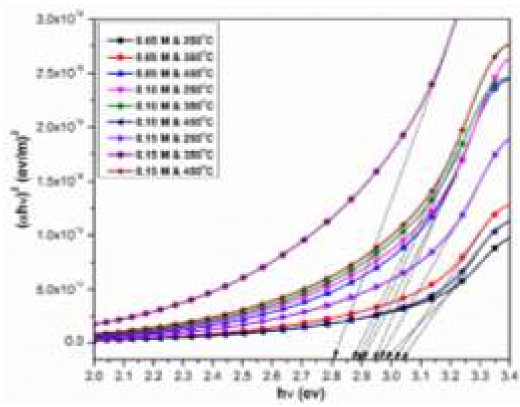

Fig. 5. The band gap energy of ZnO thin films for different mole concentrations and annealing temperatures

From the optical transmittance curves, the optical band gaps of the nanocrystalline ZnO films are evaluated. The optical absorption (α) related to the optical band gap of the prepared films at different annealed temperatures with different mole concentrations satisfies the following relation (5) [12, 16],

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$$\alpha h\upsilon^2 = B(h\upsilon - E_g) \quad (5)$$

A typical plot is presented in Fig. 5. It can be observed that the plot is linear in the region of strong absorption i.e. near the fundamental absorption edge seen at the ultraviolet region. The linear intercept at the hv-axis indicates that the directly allowed band gap values are varied from 2.80 to 3.03 eV. The estimated values for ZnO and are in good agreement with the previously reported values [1]. Further, the ZnO film annealed at 450°C with 0.10 M has a maximum band gap of 3.03 eV with the preferred orientation along (002) plane. The rise of the deposition temperature improves the transmittance of ZnO thin films. This effect may be due to the decrease of oxygen vacancies [17].

E. Electrical Properties of ZnO Thin Films

I-V measurements of ZnO thin films prepared for different mole concentrations and annealed temperatures were taken at room temperature using Keithley electrometer through two probes. The current values were measured for different applied voltages from 10 to 100 V (Fig. 6). The dc conductivity (σ) for ZnO films was calculated using the given equation (6) [12, 18],

where I is the current, V is the applied potential, d is the inter-probe distance and A is the cross-sectional area of the film.

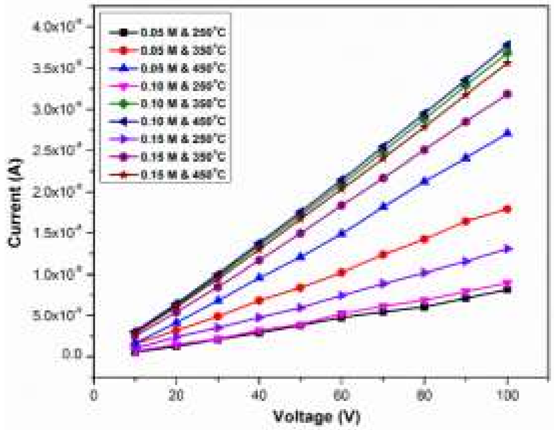

Fig. 6. The I-V characterization of ZnO thin films for different mole concentrations and annealing temperatures

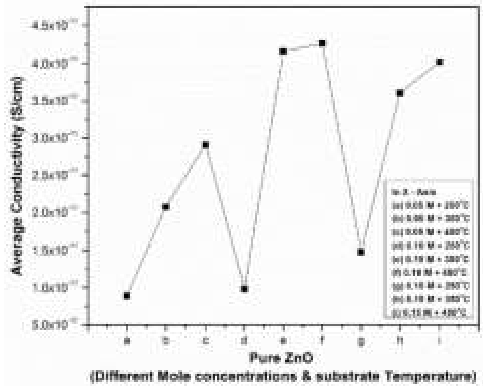

Fig. 7. The average conductivity values of ZnO thin films for different mole concentrations and annealing temperatures

Fig. 6 indicates the I-V characteristics for different mole concentrations of 0.05, 0.10 and 0.15 M and different annealed temperatures of 250, 350 and 450°C. The average conductivity values of ZnO films varied from 8.83 x 10^{-12} to 4.46 x 10^{-11} S/cm as shown in Fig. 7. The maximum conductivity value of 4.46 x 10^{-11} S/cm is obtained at 450°C with 0.10 M. The variations in conductivity values may be attributed to the oxygen vacancies in the prepared ZnO thin films [18, 19-21]. The increase in conductivity with the substrate temperature is due to the variation in morphology and the increase in grain size at 450ºC, which reduced the lattice dislocations and imperfections of the Zn–O matrix. This phenomena decreases the grain boundary volume associated with flow of charge carriers [22].

IV. CONCLUSION

Zinc oxide films have been prepared successfully using dip coating technique. The influences of the parameters like mole concentration of the precursor solution and annealing temperature of the film have been studied using structural, optical and electrical properties. 0.10 M of zinc acetate and an annealing temperature of 450°C are the optimized deposition parameters to prepare a good quality ZnO film in the present study. The XRD results show the hexagonal structure of the ZnO films with (002) as the preferred orientation along with other small peaks. The SEM results show the variations in surface of the ZnO films for varying the mole concentration at 450°C. The optical properties of the ZnO films were observed from the transmittance spectrum Maximum transmittance of 70 % and maximum band gap of 3.03 eV is observed for the films deposited at 450°C with 0.10 M. The maximum electrical conductivity value as 46 x 10^{-11} S/cm is obtained for the films deposited at 450°C with 0.10 M.

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