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2. Electrical and Structural Characterization of ZnO Thin Films Using Thermal Evaporation Technique

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Abstract

Thin films of Zinc oxide (ZnO) were prepared by physical vapour deposition method. The ZnO thin films were deposited on glass substrate at a pressure of 10^{-5} torr. This paper is aimed at studying the behavior of zinc oxide on the thin films which were annealed at different temperature for one hour in air atmosphere. The ZnO thin films were characterized by XRD (Crystalline size), scanning electron microscopy (Morphological) and elemental analysis by EDAX. The average grain size of ZnO thin films increases with increase in annealing temperature. The D.C resistance of the films was measured by half bridge method in air atmosphere at different temperatures. The ZnO thin films showed decrease in resistance with increase in temperature indicating semiconductor behaviour. The TCR and activation energy of thin films were evaluated at 450-650^{0}C temperatures.

Keywords: ZnO, PVD, thin films, XRD, FESEM, TCR

1. Introduction

In the past twenty years we have witnessed a revival of, and subsequent rapid expansion in the research on zinc oxide as a semiconductor. In recent decades, the electronics industry has predominantly focused on semiconductor and display applications [1]. The semiconductor metal oxide gas sensors like SnO_2, ZnO, WO_3 etc. have been studied due to their range of conducting variability and their strong response to reducing as well as oxidizing gases Zinc oxide is an ideal

material for fabrication of short-wavelength optoelectronic devices. It is an n-type semiconductor of hexagonal Wurtzite structure with band gap energy about 3.37 eV at room temperature with large exciton binding energy of 60 MeV [2, 3]. Higher exciton binding energy of zinc oxide enhances its luminescence property. It is cheap, nontoxic and has strong oxidizing power, high photochemical corrosive resistance, good electrical, optical and piezoelectric behavior [4].For these reasons, hexagonal wurtzite structured Zinc oxide can be used towards versatile applications in electronics [5], optoelectronic [6], transistors [7], LEDs [8], photovoltaic [9] and bio-implantable sensors [10]. A variety of thin film preparation methods have been used by the researchers to synthesize metal oxide thin films in various nano-structured forms. Some of the synthesis methods are chemical vapour deposition [4], spray pyrolysis [5], sputtering [6], activated reactive evaporation [7] etc. Physical Vapour Deposition method is straight forward and simple one because of deposition in high vacuum and at room temperature, this technique produces contamination free uniform thin films. In the present study, we used Hind Hind high vacuum depositing unit for depositing Pure Zn onto the cleaned glass substrates at room temperature.

2. Experimental Work

2.1 Preparation of ZnO Thin films

The substrates (Alumina) were cleaned liquid soap, then the substrates were put into the solution of potassium dichromate and H_2SO_4 for remove the unwanted contain. After that they are agitated ultrasonically in acetone and dried under the IR lamp. Zinc oxide thin films were prepared on the alumina substrates using physical vapor deposition method. The cleaned substrates put on the stand placed approximately 12 cm above the tungsten filament. The high purity Zinc (99.99%, 100 g) thin metal wire whose radius is 0.1 mm obtained from the Loba Chemicals Ltd. and were placed in tungsten spiral basket (filament) of the Hind High Vacuum coating unit at a pressure of 10^{-5} torr. The material was vaporized by passing the appropriate current to the tungsten spiral basket. When the temperature on the material is increased in vacuum, then the metal zinc is vaporized and the atoms of zinc get transported towards the substrates where they get deposited. The deposited Zinc thin films were placed in muffle furnace for the process of oxidation and stoichiometry of the films in different annealing temperatures [11].

2.2 Material Characterization

The ZnO thin film material is characterized by X-ray diffraction technique [Bruker D-8 model, Advance CuKα (λ=1.542AU) radiation] for structural analysis, degree of crystallinity and

grain size determination for Braggs angle (2θ) from 20 to 80 degree. The average grain size was determined by using Debye Scherer formula [12].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad \text{...............(1)}$$

where D is the grain size, λ is the wavelength of the X-ray radiation (1.542 AU), θ is the angle of diffraction and β is the full angular width of diffraction peak at the half maximum peak intensity.

The electrical measurements were carried out by using the half bridge method. The electrical resistance of the ZnO thin film samples was calculated by the relation [13]. Sheet resistivity (ρ_s) of each thin film samples was calculated from the dimension of the film samples. Sheet resistivity (ρ_s) = ρ/t, where ρ = resistivity of ZnO thin film resistors, t = thickness of the thin film samples. The effect of temperature on the resistance was studied to determine the TCR and calculated as

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) /^{o}C \quad \text{..... (2)}$$

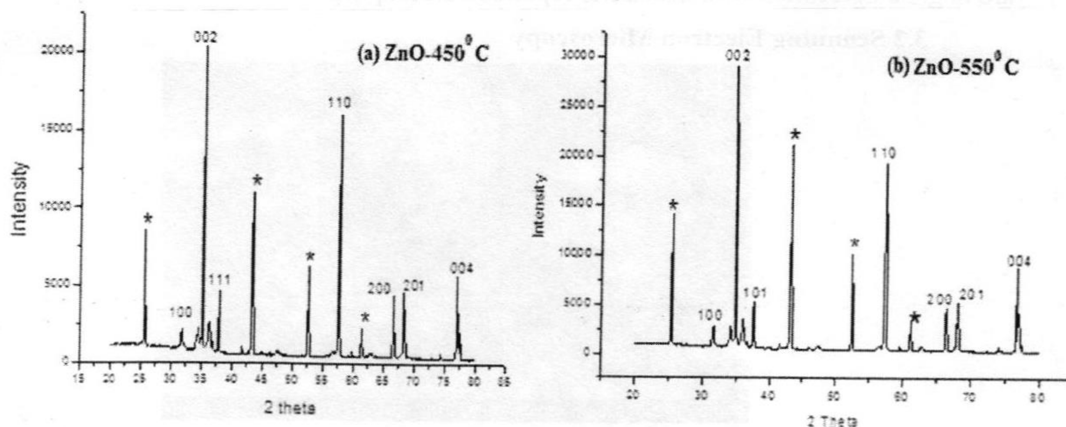
Where ΔR = change in resistance between temperature T_1 and T_2, ,ΔT = temperature difference between T_1 and T_2, R_o = Initial resistance of the film sample. Using Arrhenius relation, the activation energy of thin film samples were evaluated

$$R = R_o e^{-\Delta E/KT} \quad \text{.......... (3)}$$

Where R_o is constant, ΔE is the activation energy of the electron transport in the conduction band, K is Boltzmann constant and T is Absolute temperature.

3. Result and Discussion

3.1. X-ray Diffraction Analysis of ZnO thin Films



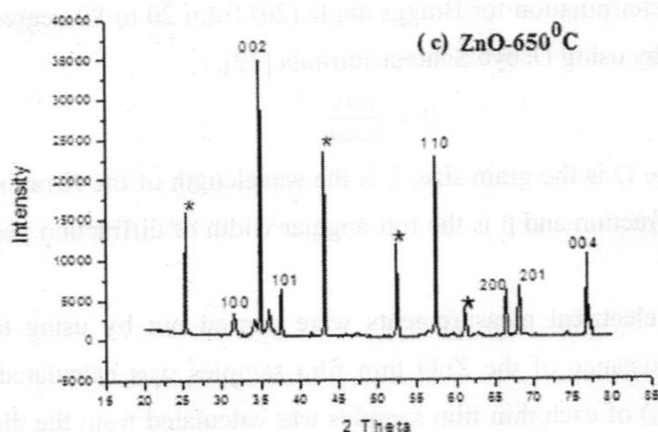


Fig.1. XRD pattern of ZnO thin films at (a) 450°C (b) 550°C & 650°C

Figure 1 shows an XRD pattern of ZnO thin films annealed at 450-650°C plotted in the range 20-800 (2θ). The XRD pattern shows several peaks of Zinc oxide phases indicating polycrystalline nature. The observed peaks of ZnO match well with reported ASTM data confirming polycrystalline structure. The sharp peaks reflexes seen on the pattern indicate that a transformation to a highly ordered crystallite has occurred in the material. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size can be attributed to the agglomeration of particles. It is observed that as the annealed temperature increases, the major contribution towards hexagonal wurtzite phase also increases In XRD pattern the observed phases of ZnO are hexagonal wurtzite structure [ASTM Card, 36-1451,34-1415], The average grain sizes for the film samples calculated by using Scherer formula [12] are found to be 48.50, 51.09, 52.00 nm (±2nm) at 450, 550 and 650°C (±2 OC) respectively, which are in good agreement with the earlier reported values. [14]

3.2 Scanning Electron Microscopy

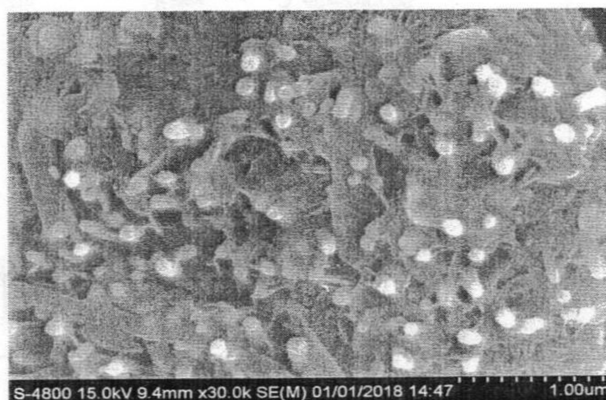


Fig. 2. Typical FESEM image of ZnO thin films annealed at 650°C

Figure 2 shows the typical SEM micrographs of ZnO thin film deposited on glass substrate fired at 650^0C for studying the surface morphology. The SEM micrographs of ZnO thin films fired at 650^0C shows polycrystalline structure with number of pores distributed on the surface of the film, basically due to evaporation of organic solvent during the firing of the films. The average particle size being 157nm at 450^0C was observed for the ZnO doped SnO_2 thin films deposited on glass substrate. The average particle size of ZnO thin films at 650^0C is 128nm.

3.3 EDAX Analysis

Figure-3, the film surface is porous and irregular of ZnO thin films annealed at 550^0C due to vaporization of material and nucleation, growth and adhesive substrate phenomena and the film is developed by oxidation process during annealing. It is observed that, the weight and atomic percentage of element increased with increased in annealing temperature. It means good oxidation has been achieved.

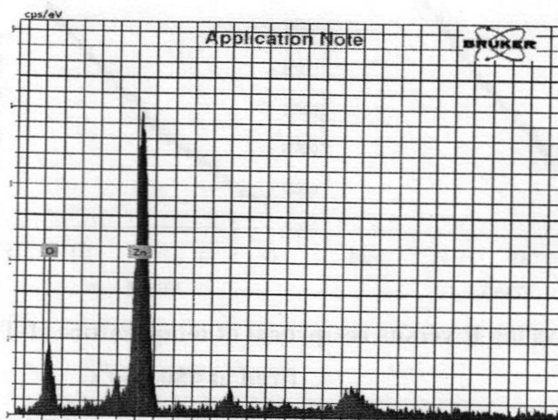


Fig. 3. Typical EDAX of ZnO Thin Films Annealed at 550^0C

3.4 Electrical Analysis of Zno Thin Films Annealed at Different Temperatures

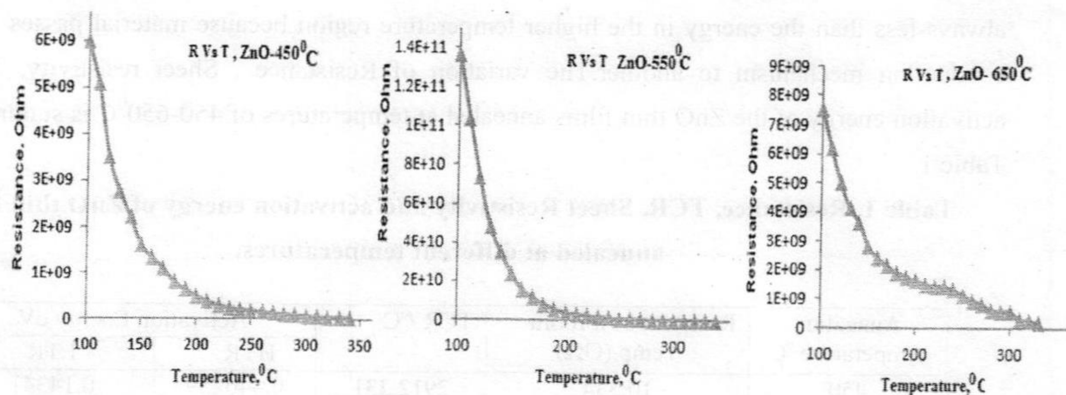


Fig.4 (a) shows the resistance variation of ZnO thin films fired at 450-650^0C.

The DC resistance of the ZnO thin films annealed at 450-650^{0}C, was measured by using half bridge method as a function temperature. The resistance of ZnO thin films decreases with increase in temperature showing semiconducting behavior. Figure 4(a) shows the resistance variation of ZnO thin films fired at 450-650^{0}C temperatures in air. ZnO thin film samples exhibited three regions of resistance similar to SnO_2 thick film Sensors. The plot shows different conduction region: (i) continuous fall of resistance, (ii) an exponential fall region and (iii) finally saturation region. Any increase in temperature of thin film causes the electrons to acquire enough energy and cross the barrier at grain boundaries [15]. There is a decrease in resistance with increase in temperature indicating semiconducting behavior, obeying $R=RO\ e^{-\Delta E/KT}$ in the temperature range of 50 to 400^{0}C.

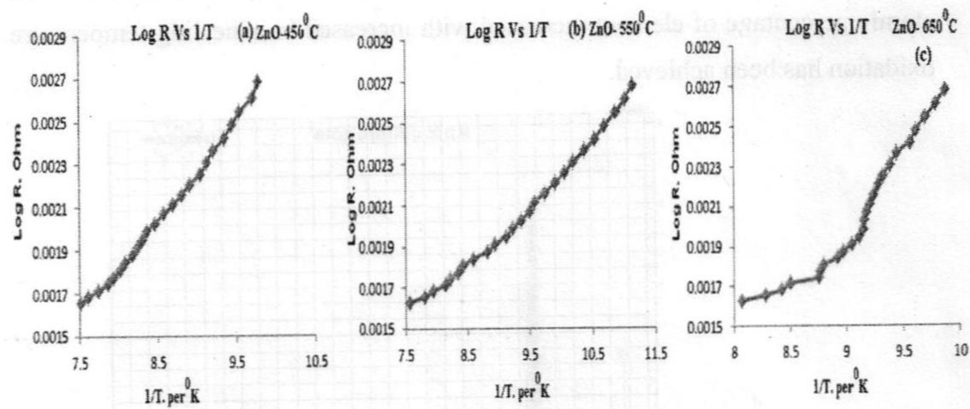


Fig.4. (b) shows log R versus reciprocal of temperature (1/T) variation of ZnO thin films fired at 450-650^{0}C

Figure 4 (b) shows log R versus reciprocal of temperature (1/T) variation of ZnO thin films fired at 450-650^{0}C. This variation is reversible in both heating and cooling cycles obeying the Arrhenius equation R=Roe-ΔE/KT. The activation energy in the lower temperature region is always less than the energy in the higher temperature region because material passes from one conduction mechanism to another.The variation of Resistance , Sheet resistivity, TCR and activation energy of the ZnO thin films annealed at temperatures of 450-650^{0}C is summarized in Table 1.

Table 1. Resistance, TCR, Sheet Resistivity and activation energy of ZnO thin films annealed at different temperatures.

Annealing temperature °C	Resistance At room Temp.(GΩ)	TCR /°C	Activation Energy eV	
			HTR	LTR
450	10.334	2912.331	0.446259	0.14341

550	6.597	3270.12	0.30698	0.12230
650	9.676	4618.564	0.286498	0.10678

Conclusions

Zinc oxide thin films were prepared by physical vapor deposition method at room temperature in vacuum atmosphere. XRD analysis shows the structure of ZnO thin films is polycrystalline in nature. The average grain size of ZnO thin films increases with an increase in annealing temperature. TCR increases with an increase in annealing temperature. It also shows voids between the particles basically due to evaporation of the organic solvent during the annealing of the thin films.

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