International Journal of Engineering and Applied Sciences (IJEAS)
ISSN: 2394-3661, Volume-3, Issue-7, July 2016

Optical and electrical properties of RF magnetron sputtered ZnO thin films deposited at different substrate temperatures

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Abstract— **Zinc oxide (ZnO) thin films were deposited on glass substrates by radio frequency magnetron sputtering using pure zinc oxide target. The effect of substrate temperature on the structural, morphological, optical and electrical properties of ZnO films were systematically investigated by X-ray diffraction, UV-Visible spectrophotometer and Hall effect measurements. All these films exhibited strong (002) diffraction peaks corresponding to hexagonal wurtzite structure. The ZnO films formed at substrate temperature of 473K exhibited optical transmittance of 93% and electrical resistivity of 6.8×10^{-2} Ω cm.**

Index Terms — **Zinc oxide; RF magnetron sputtering; substrate temperature; optical properties; electrical properties.**

I. Introduction

Zinc oxide (ZnO) is a wide band gap direct semiconductor having band gap of 3.37 eV at room temperature. It also possess large exciton-binding energy of 60 meV. ZnO is an attractive semiconductor due to its low cost, nontoxicity, high stability and high transparency in the visible wavelength. It is a promising material for many applications in toxic gas sensors [1] , solar cell windows[2], blue and ultraviolet (UV) light emitting devices[3], transparent conductors[4], surface acoustic devices[5], photovoltaic devices[6], etc.

In recent years a wide range of preparation methods such as RF magnetron sputtering [7], reactive thermal evaporation [8], spray pyrolysis [9], chemical vapor deposition (CVD)[10], molecular beam epitaxy (MBE)[11], pulsed laser deposition (PLD)[12], sol–gel process[13], electro-deposition[14], etc., have been employed for the preparation of ZnO thin films. Among the above mentioned techniques radio frequency (RF) magnetron sputtering has been found to be more effective for the deposition over large area with uniform thickness, better reproducibility, good adhesion to the substrate, good stoichiometry, high deposition rates and easy control of the composition of the films. In this technique there is a wide scope in varying the deposition parameters such as substrate temperature, partial pressure of oxygen, sputtering power, sputtering pressure in the chamber, substrate bias voltage and thickness of the film. These parameters have profound influence on the physical properties of ZnO thin films.

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In the present investigation, an attempt has been made to prepare zinc oxide thin films using RF reactive magnetron sputtering technique and to investigate the effect of substrate temperature on the structural, optical and electrical properties.

II. Experimental details

A. *ZnO thin film deposition*

ZnO thin films were deposited on ultrasonically cleaned slides of glass substrates using RF magnetron sputtering. Pure zinc oxide of 99.99% purity with 2 inch diameter and 3 mm thickness was used as a target. The deposition equipment and its construction details are discussed elsewhere [15].The zinc oxide target mounted on top of the sputter chamber so that the sputtering can be performed by sputter down configuration. The deposition chamber was maintained at a vacuum of 5 x 10^{-6} mbar before introduction of the Argon gas into the deposition chamber. Pure argon was used as sputter gas. Mass flow controllers of MKS make was used to measure the flow rates of argon gas. The zinc oxide sputtering target was pre-sputtered for 15 min. to remove any contamination on the surface of the target. During the process of film deposition sputtering power and sputtering pressure was maintained constant with varying substrate temperature. The operating conditions in the sputtering process were tabulated in Table (1).

B. *Characterization*

The crystallinity of the films was investigated by X-ray diffraction measurements technique (Philips X'Pert X-Ray Diffractometer) in the 2θ range of 20°- 80° using CuK_{α} radiation of wavelength λ=1.5406 Å at room temperature. X-ray tube was operated at a voltage of 40 kV and current of 30 mA with scanning speed of 0.5 degree per minute. Optical transmittance spectra of the films were recorded using an Analytical Technologies Limited UV-Vis spectrometer over wavelength range from 200 to 1000 nm. The electrical resistivity and Hall mobility were studied by employing the van der Pauw method [16].Quartz crystal thickness monitor was used for the measurement of thickness of the deposited films. In this work the thickness of the deposited films was maintained a constant value of 200 nm.

III. Results and Discussion

A. Deposition rate

Fig.1. shows the dependence of deposition rate as a function of substrate temperature. The deposition rate of the films was decreased from 2.9 Å/s to 0.9 Å/s as substrate temperature increased from room temperature to 673K. At lower substrate temperature, the deposition rate was high due to the lower adatom mobility on the substrate surface. The decrease in deposition rate with substrate temperature may be due to the balance between the number of atoms arriving on the substrate surface and the atoms leaving from the substrate surface by re-evaporation [17].

Table 1: Deposition parameters maintained during the deposition of ZnO films by RFmagnetron sputtering technique at various substrate temperatures.

Sputtering target	ZnO (99.99%)
	2-inch diameter and 3 mm thickness
Target to substrate distance	70 mm
Substrate	glass
Ultimate pressure	5 x 10^{-6} mbar
Sputtering pressure	3 x 10^{-2} mbar
Substrate temperature	RT to 673K
Sputtering power	100 W

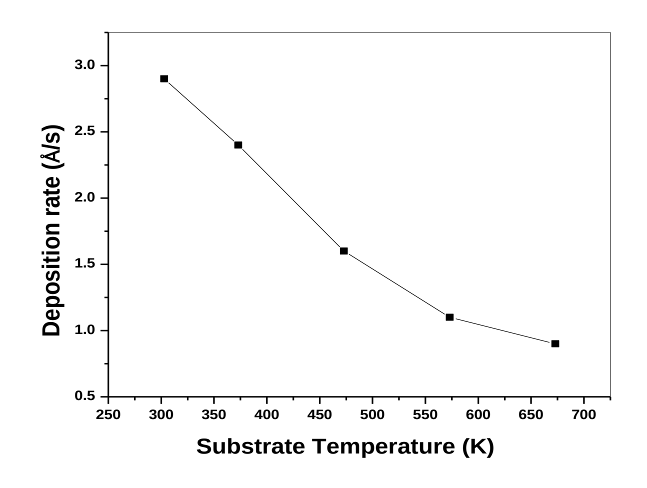

Fig.1. Variation of deposition rate as a function of substrate temperature.

B. Structural properties

Fig.2. Shows the XRD pattern of ZnO thin films grown at different substrate temperatures. The crystal structure of the films deposited at various substrate temperatures was identified to be polycrystalline nature with wurtzite structure. The position of (0 0 2) peak shifts monotonically from 34.04° for the film deposited at room temperature to 34.25° for the film deposited at 673K. The c-axis (0 0 2) peak orientation and the crystallinity were poor for the film grown at room temperature and it improved as the substrate temperature was increased upto the temperature of 673K. The films deposited on unheated substrate has low atomic mobility and tends to form preferred crystallite structure, on increasing the substrate temperature, adsorbed atoms gain extra thermal energy and have the motivity to move to another preferred sites [18]. The intensity of (0 0 2) peak decreases while the intensity of (1 0 1) increases when the substrate temperature was at 673K. The development of a (1 0 1) texture at higher substrate temperatures has also been observed by F. Wu et al. [19] for ZnO:Ga thin films.

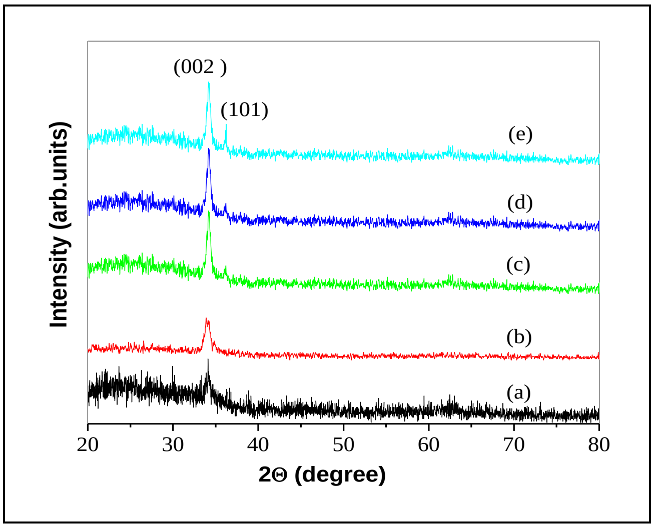

Fig.2. X-ray diffraction patterns of ZnO thin films deposited at different substrate temperatures.
(a) RT (b) 373K (c) 473K (d) 573K (e) 673K.

C. Optical properties

Fig.3. shows the optical transmittance spectra of ZnO films grown under different substrate temperatures. The average optical transmittance of the films increased from 84% to 93% in 400–800 nm range with increase of substrate temperature from RT to 473K. Further increasing the substrate temperature to 673K the transmittance of the films decreased to 86%. It was observed that the absorption edge was shifted towards shorter wavelength side with increase of substrate temperature up to 473K. The increase in transmittance of the films was related to an increase in grain size of the films.

The optical band gap energy of ZnO thin films was estimated using the Tauc's method [20]. The absorption coefficient (α) was calculated using the relation

$$\alpha = -\frac{1}{t}\ln(T) \qquad (5)$$

where "t" and "T" are the film thickness and transmittance respectively. The absorption coefficient (α) and the incident photon energy (hν) is related by the following relation

$$(\alpha h\nu) = A(h\nu - E_g)^n \qquad (6)$$

where A is a constant , E_g is the optical band gap of the material and the exponent n depends on the type of transition. n = 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect, respectively. We have calculated the direct optical band gap (E_g) by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the straight line portion of this plot to the energy axis. Fig.4. is the plot of $(\alpha h\nu)^2$ versus hν . The linear dependence of $(\alpha h\nu)^2$ to hν indicates that ZnO films are exhibiting direct band transitions. The photon energy at the point where $(\alpha h\nu)^2$ is zero is optical band gap (E_g). The optical band gap of the films increased from 3.26 eV to 3.41 eV with the increase of substrate temperature from RT to 473K. Further increasing

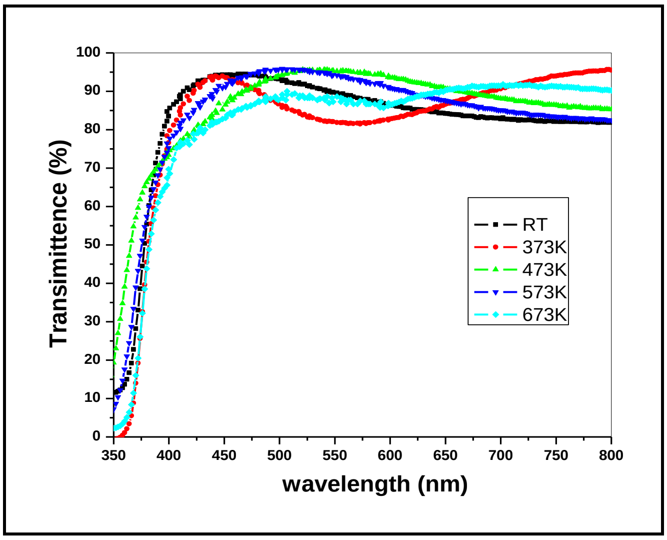

Fig.3. Optical transmittance spectra of ZnO films at different substrate temperatures.

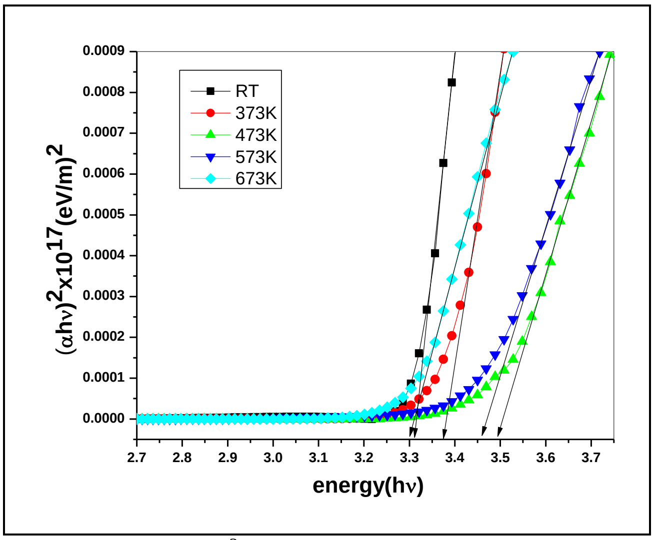

Fig.4. Plot of $(\alpha h\nu)^2$ versus hν for the ZnO films at different substrate temperatures.

the substrate temperature to 673K the optical band gap energy of ZnO thin films was decreased to 3.31 eV. Earlier reported band gap energy for ZnO films were in the range of 3.25 eV to 3.45 eV [21, 22, 23, 24, 25], which were in good agreement with our results. The average optical transmittance and band gap calculated at different substrate temperatures were summarized in Table (2).

Table 2: Optical information of RF magnetron sputtered ZnO films at various substrate temperatures.

Substrate temperature (K)	Transmitance (%)	Optical band gap (eV)
RT	84	3.31
373	88	3.37
473	93	3.48
573	87	3.45
673	86	3.30

D. Electrical properties

The sheet resistance measurement was carried out by a standard four-probe technique. The film resistivity (ρ) was determined by taking the product of sheet resistance (R_S) and film thickness (t). The Hall parameters of the films such as Hall coefficient (R_H), carrier concentration (n) and Hall mobility (μ) were determined using the following relations.

The Hall coefficient (R_H) was derived from the relation,

$$R_H = \frac{V_H t}{BI} \quad (7)$$

where 'V_H' is the Hall Voltage, 't' is the thickness of the film, 'B' is the magnetic field (8000 Gauss) applied perpendicular to the film surface and 'I' is the current passed through the film.

The carrier concentration (n) was derived from the relation,

$$n = \frac{1}{e \times R_H} \quad (8)$$

where 'R_H' was the Hall coefficient and 'e' was the absolute value of the electron charge.

The carrier mobility (μ) was determined using the relation,

$$\mu = \frac{1}{ne\rho} \quad (9)$$

All measurements were done at room temperature.

Table 3: Electrical parameters of RF magnetron sputtered ZnO films at various substrate temperatures.

Substrate temperature (cm-3) (K)	Resistivity (ρ) (Ω-cm)	Carrier concentration (n) (cm-3)	Mobility(μ) (cm2V-1s-1)
RT	1.9×10^{-1}	2.9×10^{18}	11
373	1.2×10^{-1}	3.2×10^{18}	15
473	6.8×10^{-2}	4.1×10^{18}	22
573	9.4×10^{-2}	3.1×10^{18}	21
673	1.3×10^{-1}	2.6×10^{18}	18

The electrical properties of the films were highly influenced by substrate temperature. Fig.5. shows the electrical resistivity, carrier concentration and mobility of ZnO films as a function of substrate temperature. The electrical resistivity of the films decreased from 1.9×10^{-1} Ω-cm to 6.8×10^{-2} Ω-cm with the increase of substrate temperature from RT to 473K.This decrease in electrical resistivity may be due to the improvement in the crystallinity of the films that is the increase of grain size as revealed by X-ray diffraction data. The Hall effect measurements indicates that the films were shown to be n-type conductivity. The carrier concentration of the films increased from 2.9×10^{18} cm^{-3} to 4.1×10^{18} cm^{-3} with the increase of substrate temperature from RT to 473K. Further increasing the substrate temperature to 673K the carrier concentration of ZnO thin films was decreased to 2.6×10^{18} cm^{-3}. The Hall mobility of the films continuously increased from11 $cm^2V^{-1}s^{-1}$ to 22 $cm^2V^{-1}s^{-1}$ with the increase of substrate temperature from RT to 473K. The increase of carrier mobility and concentration may be due to the improvement in the alignment of grains at the grain boundaries so that it minimizes the trapping and scattering of charge carriers at the grain boundaries [26]. The achieved results were comparable to that of the reported values of dc magnetron sputtered films [27]. The detailed Hall Effect measurements data was tabulated in Table (3).

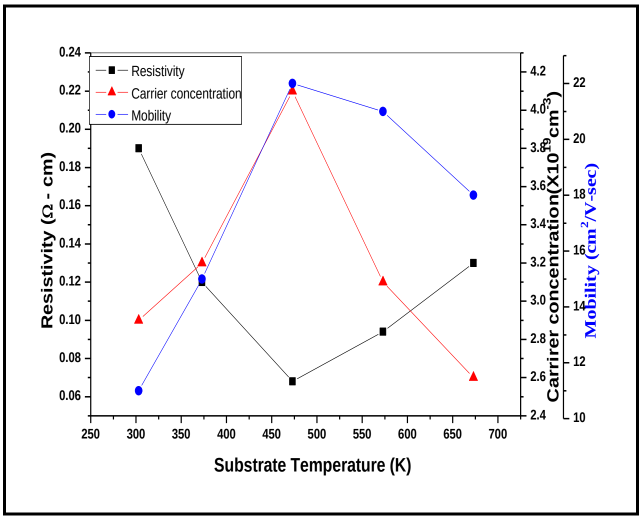

Fig.5. Variation of electrical resistivity, carrier concentration and mobility with substrate temperature.

IV. CONCLUSION

The ZnO thin films were successfully deposited by RF magnetron sputtering at different substrate temperatures. The physical properties of the films were highly influenced by the substrate temperature. The highest transmittance about 93% with optical band gap 3.41 eV and lowest electrical resistivity of 6.8×10^{-2} Ω cm was observed at substrate temperature of 473K.

ACKNOWLEDGMENT

The authors thank the Head, Department of physics, Osmania University, Hyderabad for providing necessary experimental facilities. The authors are grateful to Prof. O. M. Hussain, Department of Physics, Sri Venkateswara University, Tirupati for providing the electrical measurements. One of the authors (GAK) thank UGC, New Delhi for awarding the SRF under the UGC scheme of RFSMS.

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