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MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION 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 and morphological characterization of ZnO films were systematically investigated by X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy and atomic force microscopy. The micro structural parameters, such as the lattice constant, crystallite size, stress and strain were calculated. All these films exhibited strong (002) diffraction peaks corresponding to hexagonal wurtzite structure. Atomic force microscopy studies showed that these films were very smooth with root mean square roughness of 3.64 nm. The ZnO films formed at substrate temperature of 473K exhibited lowest stress and dislocation density.

KEYWORDS: Zinc oxide; RF magnetron sputtering; substrate temperature; structural and morphological properties.

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.

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 and morphological properties.

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MATERIALS AND METHODS

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).

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. The surface morphology was studied by Atomic Force Microscope and scanning electron microscope (SEM) of model EVO 18 manufactured by Carl Zeiss, for which an EDS is attached of model INCA,X-act manufactured by Oxford Instruments was used for composition analysis. 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.

Subheading

RESULTS AND DISCUSSION

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 [16].

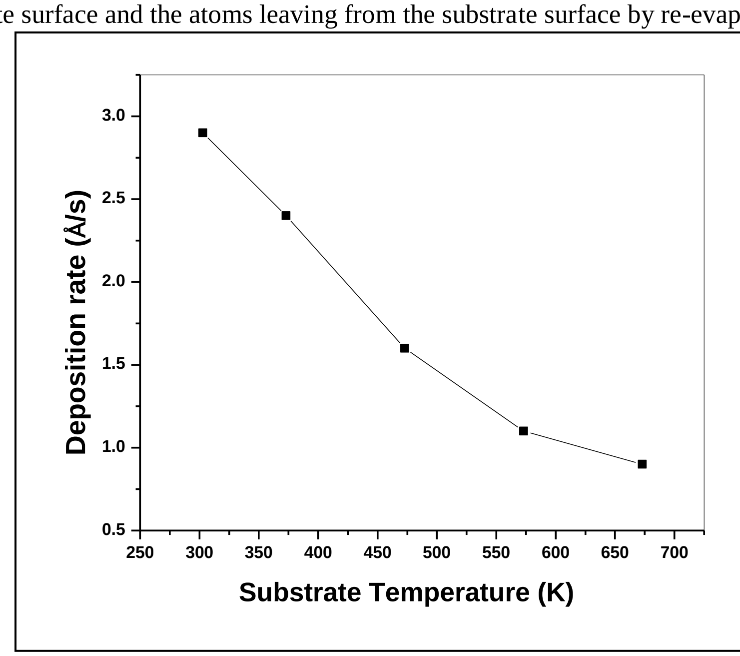

Fig.1. Variation of deposition rate as a function of substrate temperature.

Table 1: Deposition parameters maintained during the deposition of ZnO films by RF magnetron 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

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 [17].

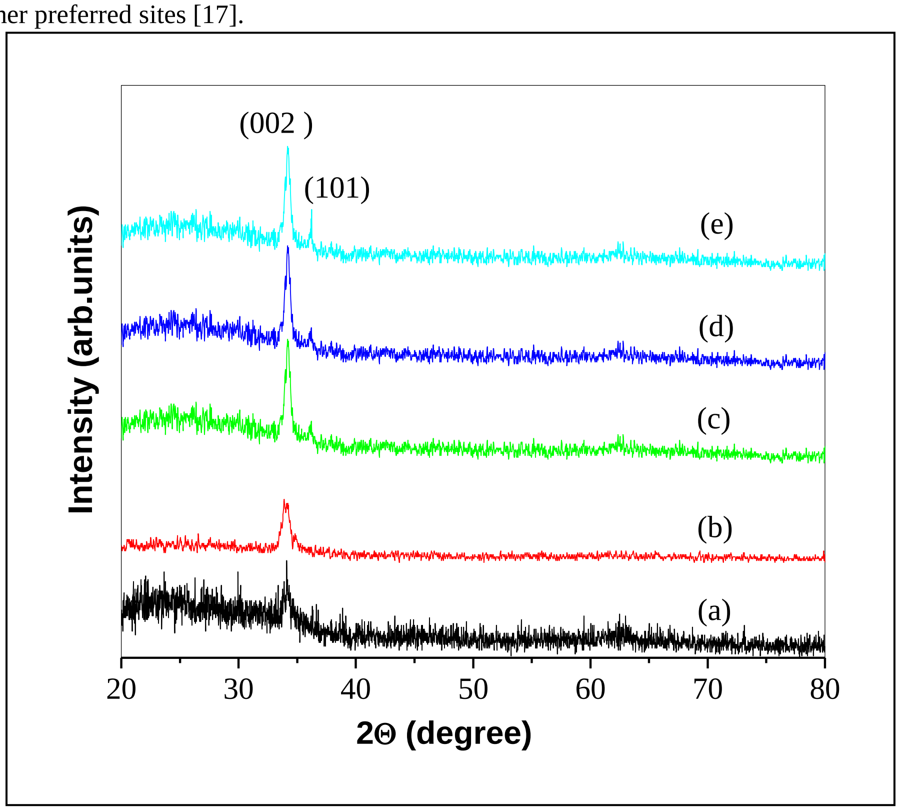

Fig.2. X-ray diffraction patterns of ZnO thin films deposited at different substrate temperatures. (a) RT (b) 373K (c) 473K (d) 573K (e) 673K.

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. [18] for ZnO:Ga thin films.

For cubic structure, lattice parameter 'a' was determined by the relation [19, 20]

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2} \quad (1)$$

where 'd_{hkl}'is interplanar spacing for planes with Miller indices (hkl).

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

Substrate temperature (K)	2θ (degree)	FWHM (degree)	Lattice parameter (nm)	Grain size (nm)	Stress (GPa)	Dislocation density (10^{15} lines/m^2)
Room temp.	34.04	0.666	0.5238	12.47	-2.696	6.426
373	34.16	0.628	0.5227	13.24	-1.739	5.702
473	34.28	0.506	0.5212	16.42	-0.434	3.305
573	34.28	0.546	0.5219	15.22	-1.043	4.314
673	34.25	0.550	0.5221	15.10	-1.217	4.384

The lattice parameter of the films was also influenced by the substrate temperature. The lattice parameter of the films increased from 0.5238 nm to 0.5212 nm with increasing the substrate temperature from RT to 473K then decreases continuously with substrate temperature for (002) peak. The present obtained lattice parameter value of 0.5212 nm at 473K was close to the standard value of 0.5207 nm. The variation in the lattice parameter with substrate temperature was due to the stresses developed in the films [21].

The crystalline size of the films was calculated for (2 0 0) peak by using Scherrer's formula [22]:

$$D = \frac{0.94 \times \lambda}{\beta Cos\theta} \quad (2)$$

where 'K' is the shape factor of a value having 0.94, λ is the wavelength of X-ray, β is full width at half maxima (FWHM) in radians and θ is the Bragg's diffraction angle.

The crystallite size of the films increased from 12.47 nm to 16.42 nm with increase of substrate temperature from RT to 473K, thereafter it decreased to 15.10 nm at 673K. The increase in the crystallite size with substrate temperature may be due to increase in the crystallinity of (002) peak.

The internal stress (σ) developed in the films was estimated from the X-ray diffraction data using the biaxial strain model [23]:

$$\sigma = \left[2C_{13} - \frac{C_{11} + C_{12}}{C_{13}} . C_{33} \right] . \left[\frac{a - a_0}{a_0} \right] \quad (3)$$

where 'C_{ij}' are the elastic stiffness constants (C_{11} = 2.1 x 10^{11} N/m^2 , C_{33} = 2.1x 10^{11}N/m^2, C_{12} = 1.2 x 10^{11} N/m^2, and C_{13} = 1.05 x 10^{11} N/m^2) and 'a' is the lattice parameter of the bulk material (0.5207 nm) and 'a_0'is the measured lattice parameter. The stress developed in the films was obtained by the shift in the interplanar spacing hence change in the lattice parameter. The negative sign indicates that the films were in a state of compressive stress. The stress in the films decreased from 2.69 to 0.43 GPa with increasing substrate temperature from RT to 473K for (002) peak. The stress developed in the films was due to the existence of microscopic voids incorporated during condensation [24].

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The dislocation density (δ) is evaluated from the crystalline size by the relation [25]

$$\delta = \frac{1}{D^2} \quad (4)$$

It has been observed that with an increase in substrate temperature the crystallite size of the films increases, in other words, dislocation density decreases. This decrease in dislocation density may be the cause for the increase in mobility with substrate temperature. The lattice parameter, grain size and stress of the ZnO films as a function of substrate temperature given in Table (2).

Surface morphology

Fig.3. indicates the scanning electron microscopy (SEM) images of the ZnO thin films grown under different substrate temperatures. The SEM images clearly indicate that the sputtered ZnO films deposited at room temperature were found to be very smooth, uniform and crack free surfaces and fine grains were appeared at substrate temperatures of 473K. The grain size decreased when the films deposited beyond this substrate temperature.

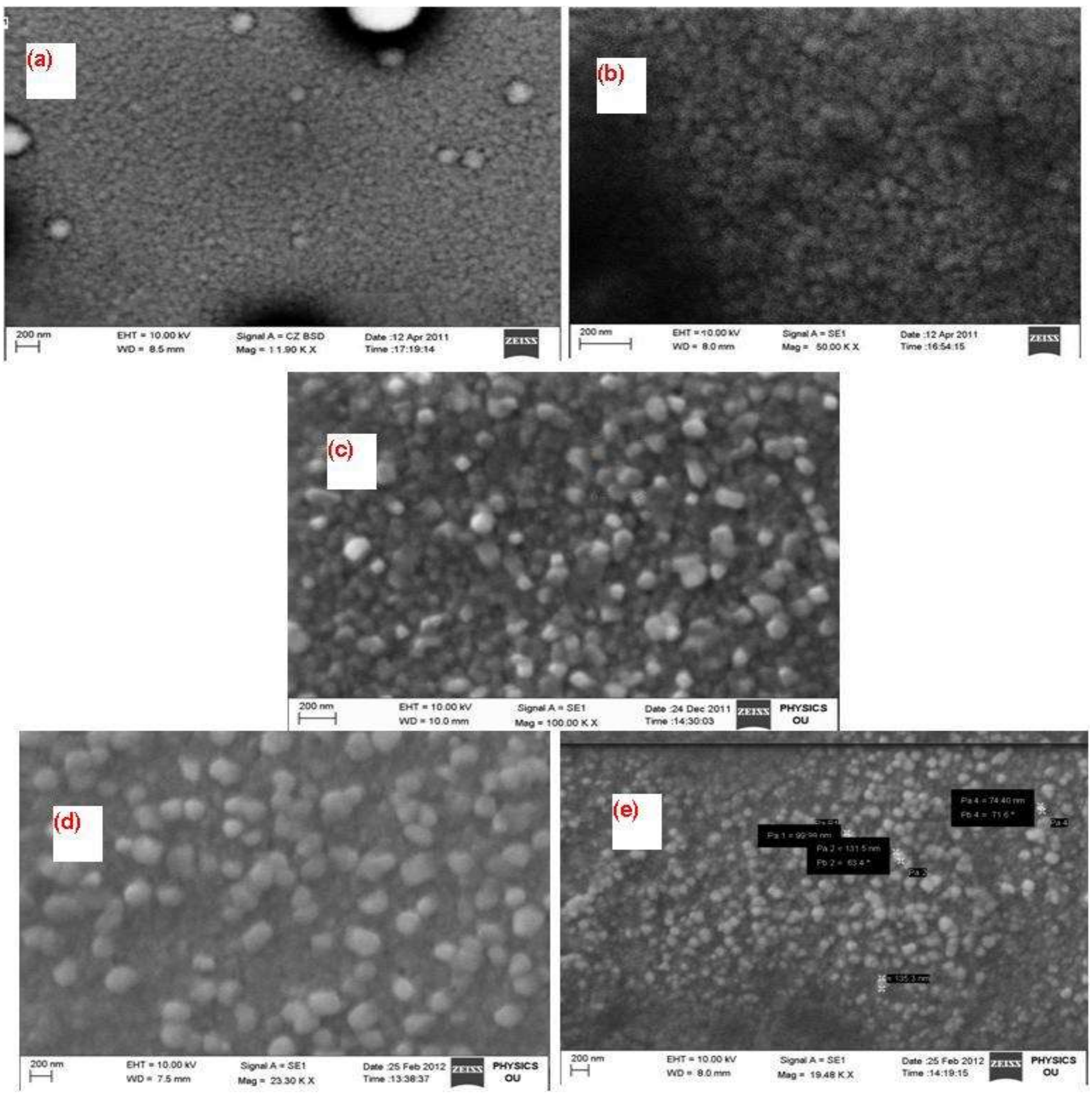

Fig.3. Scanning Electron Microscopy (SEM) images of ZnO films deposited at different substrate temperatures . (a) RT (b) 373K (c) 473K (d) 573K (e) 673K.

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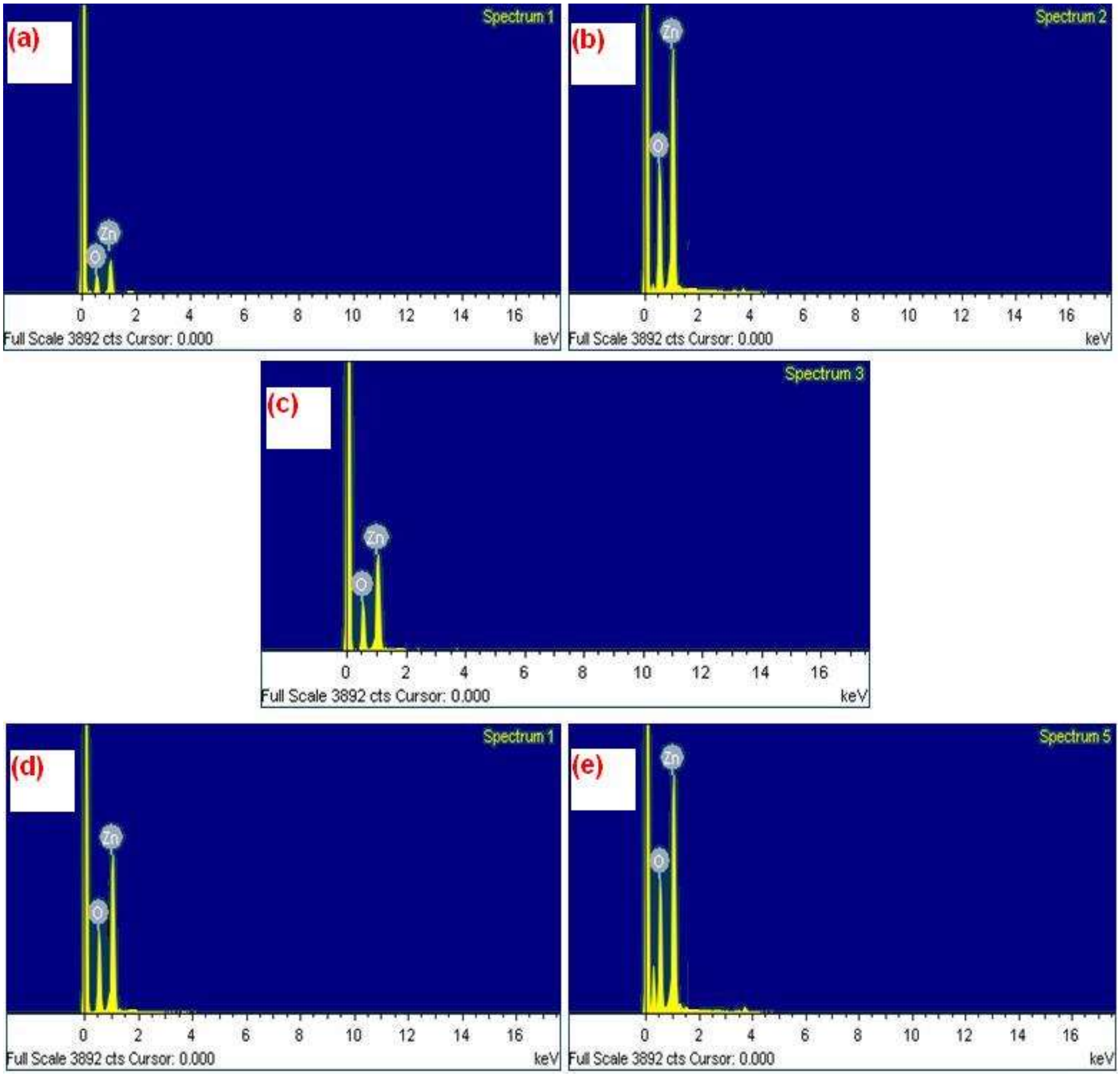

Fig.4. EDAX images of ZnO films deposited at different substrate temperatures.
(a) RT (b) 373K (c) 473K (d) 573K (e) 673K.

The chemical composition of the ZnO films grown under different substrate temperatures were determined by Energy dispersive analysis of X-rays (EDAX) and images were shown in Fig.4. EDAX analysis was given in Table (3), it revealed that all the deposited films consists of Zinc and Oxygen and the composition of the Zinc was gradually increased with substrate temperature.

The Atomic Force Microscopy (AFM) images of ZnO films grown at substrate temperature of 473K were shown in Fig.5. The root mean square (RMS) values of surface roughness for the films grown at substrate temperature of 473K was found to be 3.64 nm.

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Table 3: Compositional analysis of RF magnetron sputtered ZnO films by Energy dispersive analysis of X-rays (EDAX) at different substrate temperatures.

Substrate temperature (K)	Element	Weight %	Atomic %	Zn /O ratio
RT	O K	27.62	74.23	0.34
	Zn K	72.38	25.77	
373	O K	24.65	59.12	0.69
	Zn K	75.35	40.88	
473	O K	19.68	48.98	1.04
	Zn K	80.32	51.02	
573	O K	18.94	46.14	1.16
	Zn K	81.06	53.86	
673	O K	16.51	44.75	1.23
	Zn K	83.49	55.25	

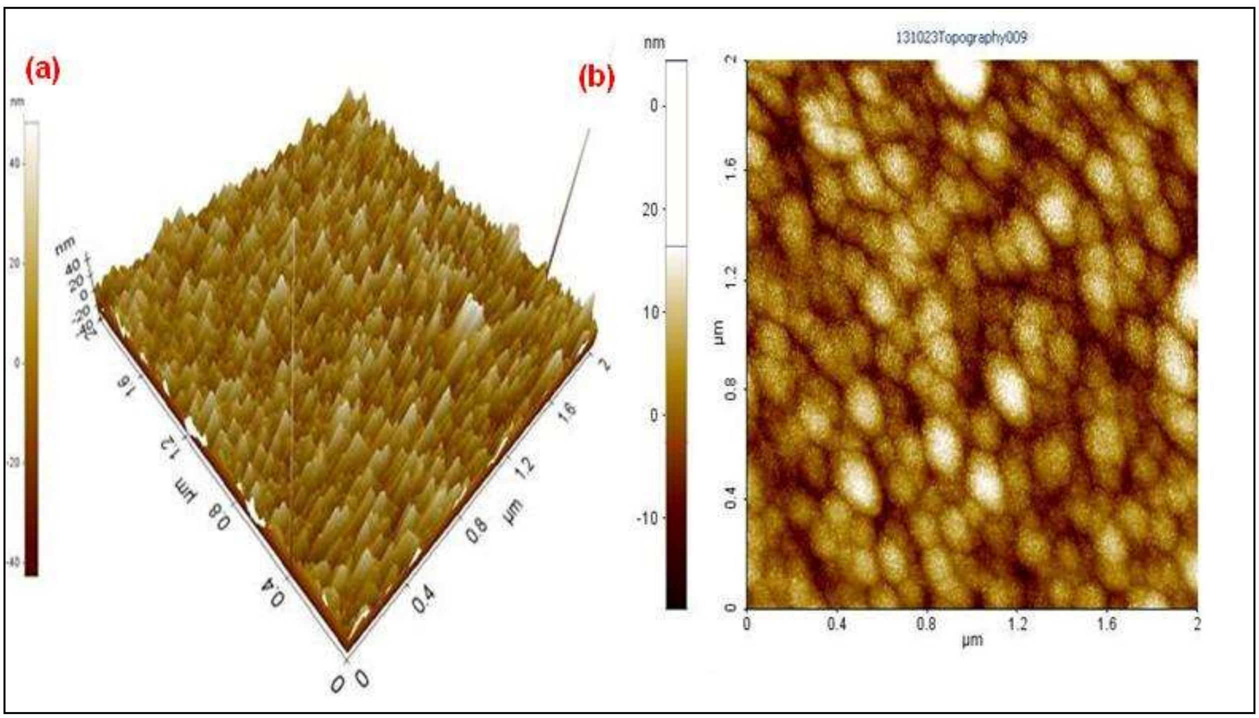

Fig.5. Atomic Force Microscopy (AFM) images of ZnO films deposited at substrate temperature of 473K.

CONCLUSION

The ZnO thin films were successfully deposited by RF magnetron sputtering at different substrate temperatures. The structural and morphological properties of the films were highly influenced by the substrate temperature. Stress free and nearly stoichiometric films with average crystalline size of 16.42 nm were obtained at substrate temperature of 473K.

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