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Influence of nitrogen annealing on the structural and electrical properties of zinc oxide (ZnO) thin film deposited by radio frequency magnetron sputtering technique

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Abstract: *Transparent conducting Zinc Oxide (ZnO) thin films with an average thickness of 130.5nm were deposited on glass substrate at room temperature by RF sputtering technique. The samples were then annealed under nitrogen atmosphere at 423K, 573K and 723K respectively. The structural and electrical properties of the films were studied using four-point probe technique, scanning electron microscopy and X-ray diffraction. The as-grown (sample that has not been annealed) was found to have a resistivity of $11\times 10^{-4}\Omega.cm$ while that of the annealed samples lies between 3.5×10^{-4} Ω.cm – 6.0×10^{-4} Ω.cm. The XRD analysis of the annealed samples shows that they are crystalline with prepared orientation of (002) plane.*
Other data analyzed include the grain size, strain and the residual stress.
Keywords:ZnO thin films,sputtering technique, structural properties,electrical properties, annealed samples.

I. Introduction

In recent years,the compound semiconductors of II-VI family such as Zinc Oxide (ZnO) has been the focus of great interest due to its availability at low cost,large exciton binding energy, energy band gap of about 3.37eV,high thermal conductivity, good transparency, high electron mobility etc. Its applications, include but not limited to, transparent electrodes in liquid crystal displays, energy saving or heat-protecting windows, electronics and optoelectronics.

Zinc oxide thin films have been prepared by various deposition methods such as thermal oxidation [19],Spin coating [10] , electron beam evaporation [20] , sputtering [3,4,14,23] , Spray pyrolysis [1,9,12,16,17,18], and chemical bath deposition [2,8].

In this paper, we report the growth mechanism and optical properties of Zinc Oxide thin film grown by RF sputtering technique. This technique is chosen because it provides a higher degree of ionization/dissociation which leads to greater oxidation rate at the substrate surface [7].In general, the advantages of sputtering are the simple apparatus, high deposition rate, low substrate temperature, good surface flatness, transparency and dense layer formation[16].

II. Experimental

2.1 Substrate preparation and thin film deposition

Prior to the deposition, the corning glass substrate were thoroughly cleaned by regular substrate cleaning method in an ultrasonic bath. This involves keeping the substrates in a dilute chemical detergent at 100^oC for 10 minutes. To remove organic contaminants, the substrates were boiled in dilute hydrogen peroxide solution for 15 minutes. The substrates were then extracted from the bath and rinsed with distilled water before being dried with nitrogen gas. The deposition chamber was thoroughly cleaned with emery paper and cotton-wool by wetting acetone and then dried with a dryer.

The ZnO target (in the form of porcelain of 4 cm in diameter) also known as the cathode is located at the upper part of the sputtering chamber. The glass substrate was placed at a distance of about 7cm from the cathode. The deposition was carried out at room temperature. Prior to deposition, the chamber was evacuated to 4.6×10^{-3} mbar.For plasma formation, research grade argon with purity 99.99% was used at a pressure range of 10^{-2}-10^{-1} mbar, oxygen was also added to facilitate the formation of ZnO on the substrate. Other deposition parameters that were kept constant include the film thickness, deposition temperature, oxygen/argon flow rate and the sputtering RF power. It has already been established that reproducible properties can only be achieved when the thickness and the deposition parameters are kept constant [9]. In all, there were four (4) samples. The films were labeled from S_1-S_4 .Sample S_4 is the as-deposited.S_1, $S_2$and S_3 were annealed under nitrogen atmosphere at 423 K,573 K and 723 K..Carbolite horizontal tube furnace was used for the annealing. The annealing was done for 60 minutes.

2.2 Measurement technique

The grown films were subjected to electrical characterization by the use of a 4-point probe. Four-point probe method is an electrical resistance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than traditional two-terminal (2T) sensing[6].A probe head with tungsten carbide tips with a point radius of 0.002", a probe spacing of 0.05" and a probe pressure of 70 to 180 grams was used for all measurements. Current was supplied by a Crytronics model 120 current source with a range of applied currents between 1μA to 100 mA. Voltages were measured by a Keithley model 181 nanovolt electrometer with an input impedance of greater than 1 GΩ. Sheet resistance (Rs in units of Ω/sq.) and resistivity (ρ in units of Ω·cm) were determined from;

$$\rho = 2\pi s \frac{V}{I} \tag{1}$$

Where S is the spacing between the probes.

The crystal structure of the films on the other hand was inspected using an X-ray diffraction performed in $2\theta/\omega$ at a voltage of 45KV and a current of 40mA.The sweeping angle was 20 to 80 degrees, the scan speed was 0.8 degrees/minute at a scan step of 0.02 and employing a $Cuk\alpha$tube ($\lambda = 0.1540598nm$) radiation. The surface morphology of the films and the micro structure were also studied.Lattice parameters were then calculated from;

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3}\frac{h^2+hk+k^2}{a^2}+\frac{l^2}{c^2}}} \tag{2}$$

where h, k and l are the Miller indices, a and c are lattice parameters

The strain in ZnO films along the c-axis is calculated from the following expression;

$$\varepsilon_{2(\%)} = \frac{c-c_0}{c_0} \times 100\% \tag{3}$$

Where c is the lattice parameter and C_0 is unstrained lattice parameter for bulk ZnO=5.2066Å

The residual stress σ in the ZnO films is determined by;

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11}+c_{12})}{2c_{13}} \frac{c-c_0}{c_0} \tag{4}$$

c_{ij} is the elastic constant for ZnO single crystals.$c_{11=208.8Gpa}$,$c_{12=119.7Gpa}$,$c_{13=104.2\ Gpa}$ and$c_{33=213.8\ Gpa}$.

The above expression reduces to;

$$\sigma = -232.8\ \frac{c-c_0}{c_0}\text{Gpa} \tag{5}$$

III. Results and Discussion

2.3 Structural Properties

Figure 1 represents the XRD pattern for S_1,S_2 and S_3 (films annealed under Nitrogen atmosphere) while figure 2 shows the XRD pattern for S_4 (as-deposited).The diffraction pattern for samples annealed at 423K,573K and 723K with peak around 32.65°,32.69° and 32.61° respectively corresponds with index (100), while the diffraction peak around 34.31°, 34.34° and 34.39° corresponding with the indexes of (002) are clearly observed. The predomination of (002) peak in the pattern proved that the ZnO films have Wurzite crystalline structure with a preferential orientation along the c-axis and without formation of any secondary phases. Increment of annealing temperature led to superior and narrower diffraction peaks which correspond with increase in crystallite size and qualities. The increase in annealing temperature increased the (002) peak intensity, while decreased those of the (100) orientation. The shift in position of the (002) peak can be attributed to better crystallinity with more relaxation caused by annealing. The values of FWHM(fullwidth at half maximum) ranges from 0.4-0.9 suggesting that nitrogen annealing caused noticeable changes in the crystallinity of the films. The shift of the (002) peak towards higher angles also implies relaxation of the residual strain introduced in the films during the deposition process. The indication that the grains are strongly oriented along the c-axis is because of the singular peak (002 at 2Θ ~ 34.31°-34.39°).This is in line with the findings of [5].

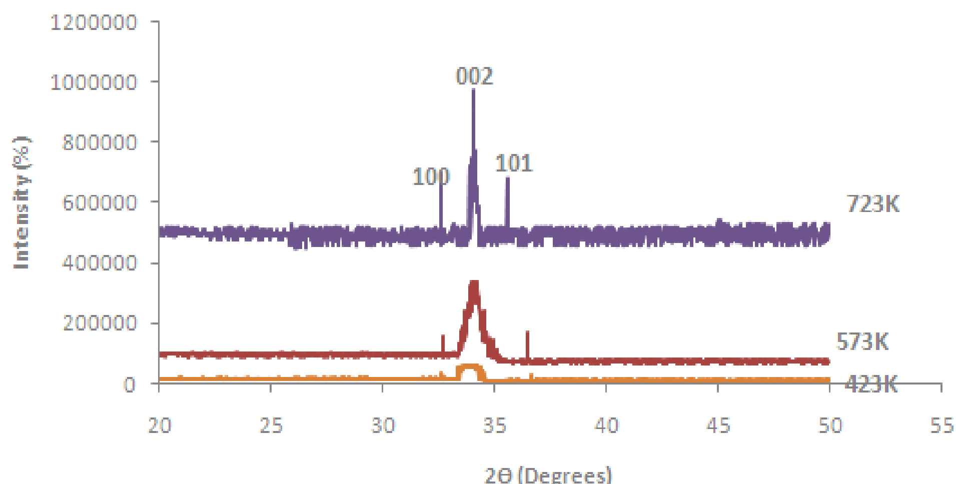


Figure 1 XRD pattern for S_1 ,S_2 and S_3

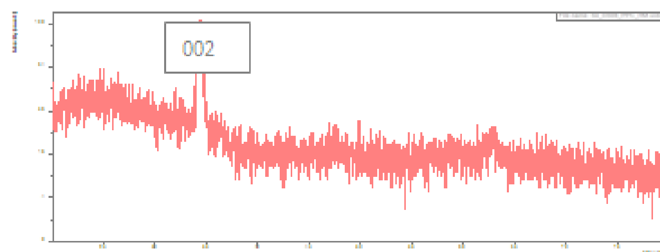


Figure 2.XRD pattern for as-deposited sample

Table 1 shows the crystallite size of the deposited ZnO thin films .It can be seen that the average value for the as-deposited sample stood at 2.5199 while that of the annealed samples stood at 2.2514 with increase in annealing temperature.

Table 1. Grain size and FWHM for as-deposited sample and those annealed in N_2 atmosphere

Sample	FWHM(2 θ)	Annealing Temp.(K)	Grain size (D)	2Θ (002) Peak only
4	0.5760		2.5199	34.12°
S_1	0.9600	423	1.5059	34.31°
S_2	0.4320	573	2.3584	34.34°
S_3	0.7680	723	2.8898	34.39°

The needle-like structure of the as-deposited sample (Figure 4) which takes different and random directions is a property of ZnO wurtzite structure. This needle-like structure has been transformed into a cloudy structure as seen in figures 5 and 6 (representing samples annealed at 423K and 573K).This is related to the decrease in the oxygen species as a result of the heat treatment under nitrogen atmosphere. For sample S_3 (Figure 7),the needle-like structure of the reference sample has been converted into columnar structure. This is caused by the high temperature in which the annealing was carried out. All the figures were magnified 5000×.

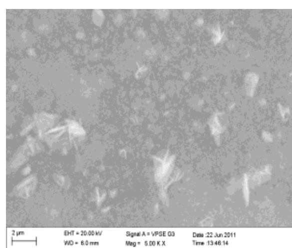


Figure 4.SEM structure of as-deposited sample

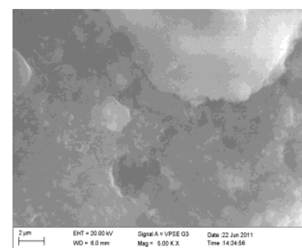
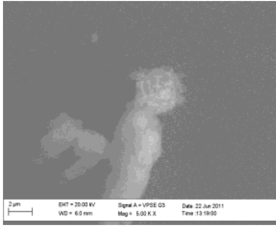


Figure 5.SEM structure of sample annealed at 423K



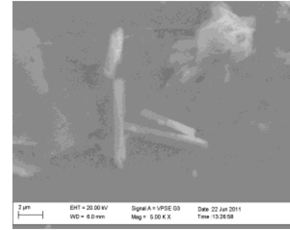


Figure 6.SEM structure of sample annealed at 423K   Figure 7.SEM structure of sample annealed at 423K

3.2 *Electrical Properties*

The resistivity of the annealed films is found to be decreasing with increasing annealing temperature.Figure 3 represents the electrical resistivity ρ (Ω.cm) with inverse of temperature for ZnO thin films.

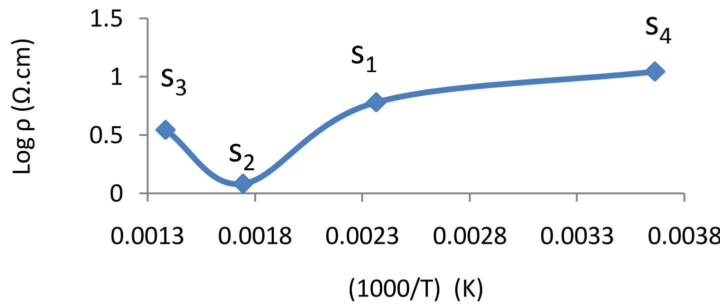


Figure 3 Plot of log ρ against (1000/T) for samples S_1, S_2, S_3 and S_4

The resistivity of the films has decreased because of the increase in carrier concentration which is caused by annealing.The observed increase in the conductivity can be correlated with the decreased concentration of grain boundaries in the films due to the presence of bigger grains and improved crystallinity which can reduce scattering processes and increase the conductivity [22].According to [13], the decrease seen for the samples was as a result of increase in carrier concentration and mobility. Furthermore the increase in carrier concentration could be attributed to crystallization of the grains into a dense structure in the film [14]. According to [6], there are two reasons for the increase in carrier concentration; first, many free electrons are caught by large numbers of traps formed by defects andsecond, when a semiconductor is abruptly terminated at the surface, the disruption ofpotential function would create discrete energy states within the band gap which were called surface states and could trap free carriers. Another reason given by [11] for the increase in conductivity of the annealed films is that due to annealing, some resistive elements such as atmospheric or air particles within the films are diminished which causes a low resistive structure of the films.

Table 2. Sheet resistance (R_S) and resistivity of as deposited sample and those annealed inN_2

Sample	Temperature(K)	Sheet resistance(R_s)Ω	Resistance(Ω.cm)
S_4	As-deposited	4.99×10^{-3}	11.0×10^{-4}
S_1	423	2.27×10^{-3}	6.0×10^{-4}
S_2	573	0.544×10^{-3}	1.2×10^{-4}
S_3	723	1.59×10^{-3}	3.5×10^{-4}

The dramatic increase in resistivity seen for sample S_3 isattributed to the decline of the carrier concentration as the annealing temperature increases. Additionally, [15] and [21] believe that this is because the number of Zn interstitials decreases probably due to Zn evaporation by increasing annealing temperature or the oxygen vacancies, which contribute the free carriers, declined by oxygen diffusion into the film with annealing treatment. Annealing in nitrogen often decrease film's resistivity because it may help grains to be recrystallized into a dense structure in the film.

Table 3. Strain and residual stress for as-deposited samples and those annealed in N_2

Sample	T(K)	ε_2 (%)	$\sigma(Gpa)$
S_1	423	1.77	4.13
S_2	573	0.50	1.18
S_3	723	0.11	0.26
S_4		0.05	0.12

IV. Conclusions

Zinc Oxide (ZnO) thin films deposited by RF sputtering technique were prepared on corning glass substrate and annealed under nitrogen atmosphere. The effects of annealing under such an atmosphere on the film's structural and electrical properties were studied in detail.The deposition temperature was maintained at room temperature.The predomination of (002) peak in the pattern proved that the ZnO films have Wurzite crystalline structure with a preferential orientation along the c-axis and without formation of any secondary phases.The shift of the (002) plane proved that the structure has been improved by annealing.The electrical resistivity decreased for all the annealed samples if compared to the as-deposited sample. The shift in the 002 peak by any value shows the existence of residual stress between ZnO and the substrate. The compressive stress can be relaxed through high temperature (RTA) process. The origin of the residual stress in the as-deposited comes about because the residual stress in ZnO films contains a thermal stress component and an intrinsic stress component. The thermal stress is due to the difference in the thermal expansion coefficient between ZnO (4.75×10^{-6}/K) and silicon (2.6×10^{-6}/K).Since the thermal expansion coefficient of ZnO is bigger than that of Si substrate,the substrate gives a resultant tensile stress effect to the ZnO films as the substrate cools down from high temperature to room temperature. Intrinsic stress has its origin in the imperfection of the crystallites during growth. Several depositions parameters, such as temperature, pressure, power and gas mixture would contribute to the intrinsic stress [23].

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