Effect of annealing on ZnO thin films grown on quartz substrate by RF magnetron sputtering

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Abstract: Zinc oxide thin films were grown on quartz substrates by RF magnetron sputtering technique in an Argon atmosphere with sputtering power of 50 W and sputtering pressure of 2x10⁻² Torr and studied the effect of annealing on the structural and optical properties. Crystalline properties of ZnO films as a function of annealing temperature were investigated using X-ray diffraction. XRD analysis revealed that the deposited films were polycrystalline in nature with strong preferential orientation of grains along the c-axis. The micro structural parameters, such as the lattice constant, crystallite size, stress and strain are calculated. The effect of annealing on the deposited films was discussed. All the films present a high transmittance of above 90% in the wavelength range of the visible spectrum and sharp absorption edge near 380 nm.

1. Introduction
Zinc oxide (ZnO), a II–VI compound semiconductor with a direct band gap of 3.3 eV, has recently received great interest as a promising candidate for the fabrication of ultraviolet (UV) light-emitting devices [1]. Its large exciton binding energy of 60 meV enables the realization of efficient exciton-related UV lasing at room temperature [2,3]. High quality ZnO thin films are therefore desirable to achieve such applications. So far, various preparation methods have been used to deposit the ZnO films, such as: RF magnetron sputtering [4], spray pyrolysis [5], chemical vapor deposition (CVD) [6], pulsed laser deposition [7], and sol–gel process [8]. Among these means, RF Magnetron sputtering is preferred due its reproducibility and for getting highly oriented films. This physical vapor deposition is used to produce films with the desired optoelectronic and nanostructure properties by precisely controlling the parameters like Ar-O₂ flux deposition pressure, target-substrate distance, RF power and substrate temperature. In the present study, we have made an attempt to produce highly textured ZnO nanocrystalline films in the absence of oxygen environment on quartz substrates using RF magnetron sputtering and studied the effect of annealing treatment on the structural and optical properties.
2. Experimental details

2.1. Substrate cleaning
The substrate cleaning is very important in the deposition of thin films. The quartz substrates were first cleaned by a mild soap solution then degreased with acetone, etched with 5% of HCl for 30 min., ultrasonically cleaned by de-ionized water and finally dried in the air.

2.2. ZnO thin film deposition
ZnO thin films were grown on quartz substrates by using RF magnetron sputtering. The sputtering system is capable of creating an ultimate vacuum of $5 \times 10^{-5}$ Torr. A power supply operated at a crystal-controlled frequency of 13.56 MHz. The sputtering chamber was pumped with turbo molecular pump and rotary pump combination. The pressure in the sputter chamber was measured using digital Pirani and Penning gauge combination. The magnetron target assembly was mounted on top of the sputter chamber such that the sputtering could be done by sputter down configuration. A high purity (99.99%) ZnO target of 2-in. diameter and 3 mm thickness was used for the sputtering. Pure argon was used as sputtering gas. The flow rate of argon gas was controlled by Tylan mass flow controller. The sputtering chamber was pumped down to the vacuum of $5 \times 10^{-5}$ Torr before the introduction of Argon gas. The target was pre-sputtered for 15 min to remove any impurity on the surface of the target. A shutter was placed between the target and substrate to control period of coating. The target was water-cooled and the substrate was kept at room temperature initially. During the film deposition, the substrate temperature was increased due to the bombardments of the sputtering ions and the final substrate temperature was nearly 40–60 °C. To measure the deposition rate and film thickness, a vibrating quartz crystal was used. The sputtering conditions maintained during the growth of ZnO films are given in Table 1. ZnO films deposited at room temperature on quartz substrate were subjected to annealing treatment in air for 2 h at temperature of 200, 400, 600 and 800 °C, respectively.

The crystalline structure of the films was studied by x-ray diffraction measurements obtained with a Philips X'Pert X-Ray Diffractometer (XRD) in the 20 range of 20°-80° using CuKα radiation of wavelength $\lambda=1.5406$ Å at room temperature. X-ray tube was operated at 40 kV (Voltage) and 30 mA (current) with scanning speed of 0.5°/min. Optical transmittance spectra of films were recorded with a SHIMADZU 3100 UV-Vis spectrometer over wavelength range from 200 to 800 nm.

3. Results and discussion

3.1. Structural properties
XRD patterns of ZnO films annealed at different temperatures are shown in Fig. 1. It is found that XRD patterns of ZnO thin films annealed at different temperatures show the same form, that is only a (002) diffraction peak is detected in the films. This indicates that ZnO films prepared by sputtering deposition show a good c-axis orientation perpendicular to the substrate and also means that orientation of prepared ZnO films is not destroyed after further annealing treatment. The diffraction peak angle of the films annealed at RT, 200, 400, 600 and 800 °C appears at 33.84°, 34.59°,

| Deposition parameters maintained during the deposition of ZnO films by RF magnetron sputtering |
|-----------------------------------------------|
| Sputtering target | ZnO (99.99%) 2-in. diameter and 3 mm thickness |
| Target to substrate distance | 70 mm |
| Substrates | quartz |
| Ar gas flow rate | 80 SCCM |
| Ultimate pressure | $5 \times 10^{-5}$ Torr |
| Sputtering pressure | $1.2 \times 10^{-3}$ Torr |
| Substrate temperature | 273K |
| Sputtering power | 50 W |
| Thickness | 100nm |
34.80°, 34.92°, and 35°, respectively. Compared with the (002) peak position of ZnO powder (2θ = 34.420), the diffraction angle of the films grown at RT decreases, which results in the increase of c-axis value. This indicates that ZnO films grown at RT suffer compressive stress along the interfaces. The diffraction angle of the films annealed at higher temperature increases in comparison with bulk ZnO, which indicates that c-axis values of ZnO films are shortened. So the stress in ZnO film shows tensile along the interfaces. The stress is related to the defects in the films, i.e., the compressive stress may be due to zinc interstitials, but the tensile stress may be due to the oxygen vacancies in the lattice of ZnO crystallites in the film. In addition to intrinsic stress originating from the defects (zinc interstitials or oxygen vacancies) in the ZnO lattice, the stress also originates from thermal stress, which results from the difference in coefficient of thermal expansion (CTE) of ZnO thin films and quartz substrate [9]. As the annealing temperature increases from 200 to 800 °C, the FWHM decreases from 0.33 to 0.14 and the crystallite sizes increases from 24 to 57 nm.

The average crystallite sizes of the films annealed at different temperature have been calculated using the Scherrer’s formula:

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) and \( \beta \) are X-ray wavelength, the Bragg’s diffraction angle and the full width at half maxima (FWHM) of the peak corresponding to the “θ” value.

Dislocation density (\( \delta \)) and Number of crystallites per unit area (N) have been calculated using the crystallite size and thickness of the film [10-12].

The average uniform strain (\( e_{zz} \)) in the lattice along the c-axis in the randomly oriented ZnO films annealed at different temperature have been estimated from the lattice parameters using the following expression [13],

\[ e_{zz} = \frac{(d-d_0)}{d_0} \]  

(2)

where ‘\( d \)’ is the lattice parameter of the ZnO film calculated from (0 0 2) peak of XRD pattern and the “\( d_0 \)” is the lattice parameter for the ZnO bulk.

For hexagonal crystals, the stress (\( \sigma \)) in the plane of the film can be calculated using the biaxial strain model [14]:

\[ \sigma = (2C_{13} - (C_{11}+C_{12}) C_{33}/C_{13}) e_{zz} \]  

(3)

Here \( C_{ij} \) are elastic stiffness constants (\( C_{11} = 2.1 \times 10^{11} \) N/m\(^2\), \( C_{33} = 2.1x \times 10^{11} \) N/m\(^2\), \( C_{12} = 1.2 \times 10^{11} \) N/m\(^2\), and \( C_{13} = 1.05 \times 10^{10} \) N/m\(^2\)). This yields the following numerical relation for the stress derived from the change in the ‘\( d \)’ lattice parameter:

\[ \sigma \left( \text{N m}^{-2} \right) = -4.5 \times 10^{11} e_{zz} \]  

(4)

Figure 1. XRD patterns of ZnO films annealed films at different temperature.

Figure 2. Optical transmittance spectra of ZnO annealed at different temperature.
Table 2: Structural information of ZnO thin films annealed at different temperature.

| annealing temperature (°C) | Lattice parameter (nm) | Grain size (nm) | Dislocation density \((10^{13} \text{ lines/m}^2)\) | Number of grains/unit area \((10^{16} \text{ m}^{-2})\) | Strain \((10^3)\) | Stress (GPa) |
|----------------------------|------------------------|----------------|---------------------------------|----------------|----------------|-----------|
| RT                         | 0.5292                 | 22.21          | 2.027                            | 0.9127         | 17.09          | -7.69   |
| 200                        | 0.5180                 | 24.77          | 1.629                            | 0.6579         | 5.18           | 2.33    |
| 400                        | 0.5151                 | 26.7           | 1.402                            | 0.5253         | 10.75          | 4.83    |
| 600                        | 0.5134                 | 21.7           | 2.123                            | 0.9786         | 14.01          | 6.30    |
| 800                        | 0.5123                 | 57.87          | 0.298                            | 0.0515         | 16.13          | 7.25    |

The various structural parameters for ZnO thin films annealed at different temperature were calculated and are represented in Table 2.

From the Table 2, it has been observed that the lattice constant decreases with increasing annealing temperature. The change in lattice constant for the thin film deposited over the bulk clearly suggests that the film’s grains are under stress and that may be due to a change in the nature and concentration of the native imperfections. This causes either elongation (tensile) or compression of the lattice parameters. The density of film is, therefore, expected to change in accordance with changes in the lattice constant. The film crystallite size increases with increasing annealing temperature. The average internal stress for the ZnO films deposited at RT is found to be compressional in nature. The negative sign indicates that the films are in a state of compressive stress. As annealing temperature increases the tensile stress increases. The microstrain \(\varepsilon\) and the dislocation density \(\delta\) are observed to exhibit a slow decreasing trend. The decrease in \(\varepsilon\) and \(\delta\) at higher annealing temperature may be due to the movement of interstitial Zn atoms from inside the crystallites to the grain boundary, which leads to a reduction in the concentration of lattice imperfections. Further, the number of crystallites decreases with increasing annealing temperature.

3.2. Optical properties

Fig. 2 shows the optical transmittance spectra of ZnO films annealed at different temperatures. All the films present a high transmittance of above 90% in the wavelength range of the visible spectrum and sharp absorption edge near 380 nm. The optical transmittance of the films increased with increase of annealing temperature. The absorption edge was shifted towards lower wavelength with the increase of annealing temperature. The increase of transmittance of the films was related to an increase in grain size of the films.

4. Conclusion

C-axis oriented ZnO films on quartz substrate have been deposited by RF magnetron sputtering technique and have been thermally annealed. Based on the result of XRD measurement, the increase of annealing temperature increases the crystalline quality, grain size and relaxes residual compressive strain. The optical transmittance of the films increased and the absorption edge was shifted towards lower wavelength with increase of annealing temperature.

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