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Deposition and characterization of sputtered ZnO films

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Abstract

Zinc oxide thin films were deposited by radio frequency magnetron sputtering at room temperature using a metallic zinc target in a gas mixture of argon and oxygen. Plasma power, oxygen/argon gas ratio, gas pressure, and substrate temperature were varied, and an experimental design method was used to optimize these deposition parameters by considering their interdependence. Crystalline structures and film stresses were examined. Post-deposition rapid thermal annealing was also carried out to observe its effects on the film properties. Statistical analysis was then used to find the optimal sputtering conditions. Results indicated that plasma power and gas pressure have the largest effects on film crystallization and stress and that postdeposition annealing can be used to improve the quality of the film properties.

Keywords: Zinc oxide; RF magnetron sputtering

1. Introduction

Among the many piezoelectric materials, zinc oxide (ZnO) is well known for its wide range of applications due to its high piezoelectric coefficient [1]. Polycrystalline ZnO possesses a hexagonal wurtzite structure and piezoelectric properties when its *c*-axis is perpendicular to the substrate [2]. Zinc oxide thin films have recently received much interest due to their versatility and potential applications to microelectromechanical (MEMS) devices. The material exhibits a large electromechanical coupling coefficient and can be deposited using various methods including: chemical vapour deposition (CVD), molecular beam epitaxy (MBE), pulsed laser deposition, spray pyrolysis, and radio frequency (RF) magnetron sputtering. Among these,

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sputtering offers advantages in that film deposition can be carried out at low temperatures while yielding preferred orientation and uniform properties.

The properties of sputtered ZnO thin films are known to depend on deposition parameters such as RF power, pressure, substrate temperature and gas atmosphere [3]. Previous work has focused on exploring the effect of these parameters on crystallinity and orientation, but many of these efforts examined the effect of individual parameters without considering the interdependence between them. In this study, experimental design methodology was used to study the significance of the interdependence between sputtering parameters by testing specific parameter combinations and then using statistical analysis to map the response surfaces. Postdeposition annealing was then used to yield ZnO films with optimal characteristics for use in microelectronic devices.

2. Experiment

The substrates were loaded into a magnetron sputtering system with a target to substrate distance fixed at 11 cm. The chamber was evacuated to a pressure of less than 1×10^{-4} Pa by a turbomolecular pump before the generation of plasma, activated by RF power at 13.56 MHz. The concentrations of Ar and O_2 were regulated using mass flow controllers. To prevent contaminants from being deposited on the substrate, the target was presputtered for 20 min. This also resulted in stability in the plasma.

ZnO thin films were sputter-deposited at room temperature using a metallic zinc target (99.99% purity) in a gas mixture of Ar and O_2. The interdependent deposition parameters investigated include: plasma power, O_2/Ar gas ratio, and gas pressure. RF power was varied between 225 and 275 W, O_2 concentration was changed between five and 25%, and pressure was varied across 0.7–1.3 Pa in a Box–Behnken design [4]. This is an independent quadratic design with parameter combinations at the center and midpoints of the edges of the process space. It requires the smallest number of runs for systems with three factors at three different levels. The deposition time for all the films was 15 min, so that the film deposition rates could then be determined.

Crystalline properties of the films were investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Film stresses were determined by substrate curvature measurements based on the Stoney equation. Measuring the change in curvature of the centre of the substrate before and after deposition allowed us to calculate the deposition-induced stress using the Stoney equation, which is given by

$$\sigma_f = \sigma_i + \sigma_{\mathrm{th}} = \frac{E_s t_s^2}{6(1 - v_s)t_f}\left(\frac{1}{R_f} - \frac{1}{R_o}\right)$$

where σ_i and σ_{th} are the intrinsic and thermal stresses, E_s and v_s are the Young's modulus and Poisson constant for silicon, t_s and t_f are the initial and final thicknesses, and R_o and R_f and are the initial and final radii of substrate curvature. Postdeposition rapid thermal annealing was also carried out for ten minutes at 400 °C in a nitrogen (N_2) gas environment. The heating and cooling down rates were constant, and it took approximately one minute for the sample to reach the annealing temperature. Annealing has previously been shown to eliminate compressive film stress and improve crystallinity [5].

3. Results and discussion

All the films exhibited preferred *c*-axis orientation. Fig. 1 shows films deposited under various conditions, all with single peaks near 34°, which corresponds to diffraction from the (002)

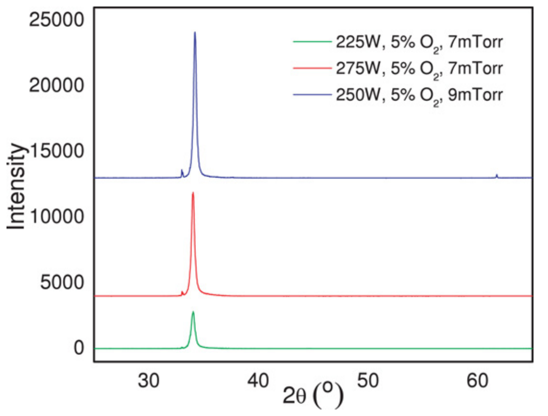

Fig. 1. XRD patterns of ZnO films sputter deposited on Si.

ZnO planes. ZnO crystals typically grow as long hexagonal rods along the *c*-axis, resulting in columnar grains that are perpendicular to the substrate. The major peak identified is comparable with JCPDS file 89-0510 (International Centre for Diffraction Data).

Crystallite sizes were calculated from the Debye–Scherrer formula: $D = \frac{K\lambda}{\beta\cos\theta}$ where K is the shape factor of the average crystallite (expected to be 0.91), λ is the X-ray wavelength ($\lambda = 0.15406$ nm for Cu target), β is the full width at half-maximum in radians, θ is the Bragg angle, and D is the mean crystallite dimension normal to diffracting planes. Average sizes varied from 15 to 30 nm. Postdeposition annealing also led to narrower diffraction peaks with greater intensity, corresponding to increases in crystallite sizes. It is also observed that while the intensities of individual sample peaks increased, their relative intensities were unchanged, indicative that annealing leads to a recovery or "precrystallization" process where strained crystallites reduce the number of defects [6].

A high deposition rate is important to the low-cost production of these films. The highest deposition rate achieved was 22.4 nm/min, allowing thick (2 μm or more) films to be deposited within a few hours. The effect of deposition conditions on the ZnO crystallite size was also studied. Higher RF power resulted in larger crystallite sizes. Increasing energy of the atoms arriving at the surface promotes grain growth. Larger crystallite sizes were also observed for increases in deposition pressure since higher pressure corresponds to an increased number of atoms arriving at the surface, promoting growth. The average crystallite sizes were significantly less than the thicknesses of the deposited films. Increasing the amount of O_2 during deposition resulted in smaller crystallite sizes. More O_2 resulted in more frequent collisions between the Ar and O_2 atoms resulting in less growth.

The microstructure of a 2 μm thick ZnO film deposited on a four-inch thick (001) Si wafer was examined using SEM. Fig. 2(a) shows a typical cross-sectional SEM micrograph, which confirms *c*-axis orientation with columnar growth that is perpendicular to the surface. This columnar growth is indicative of highly *c*-axis orientated piezoelectric quality film [7].

Atomic force microscopy (AFM) was used to examine the surface morphology and surface roughness of the films over a cross-sectional area of 1 μm^2 as shown in Fig. 2(b). Root mean square (RMS) surface roughness values for these films were less than one nanometer, indicating that the films are indeed quite smooth. It was also observed that annealing had little to no effect on the surface roughness.

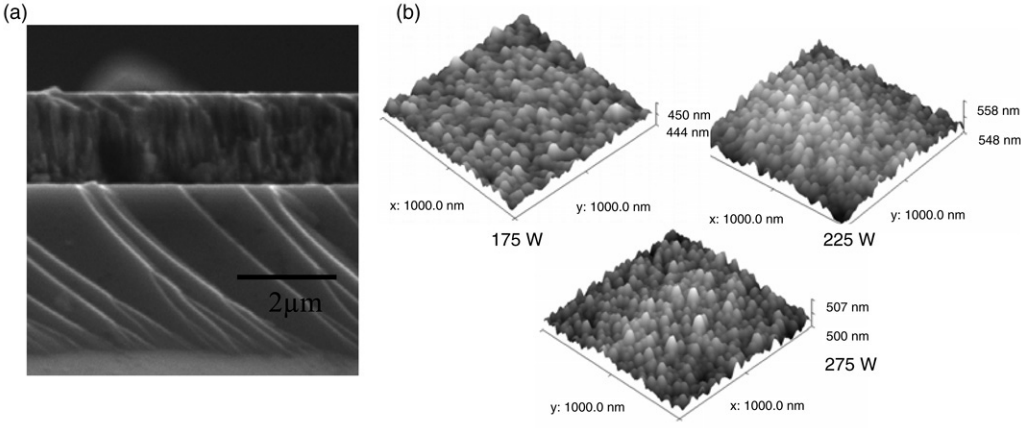

Fig. 2. (a) Cross-section of ZnO film. (b) AFM images of ZnO deposited at different RF powers.

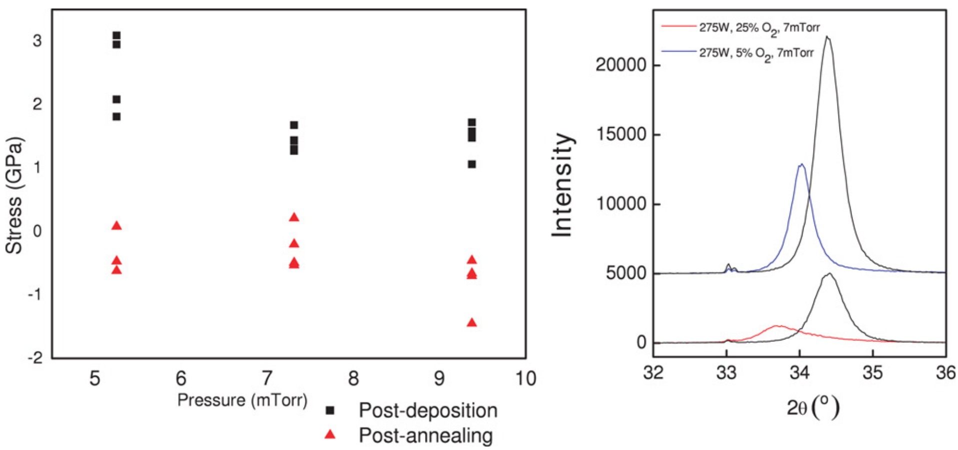

Fig. 3. (a) Changes in film stresses due to annealing. (b) Shift in XRD peaks corresponding to a relief of intrinsic stress due to annealing.

Intrinsic stress in ZnO is compressive and significantly greater than the thermal stress—values on the order of 1 GPa are typical for sputtered ZnO films. Energetic particles strike the film during deposition resulting in high atomic packing densities and large compressive stresses. The dependence of film stresses on sputtering parameters was also examined. Changes in RF power and O_2 concentration led to variation in the observed stresses, but notable statistical trends were not observed. Increasing pressure resulted in decreased compressive stress, which may be due to the formation of more porous structures.

All deposited films exhibited significant compressive stresses on the order of a few GPa, but after annealing they then exhibited tensile stresses on the order of GPa (see Fig. 3(a)). Annealing also resulted in shifting of (002) X-ray diffraction peaks to slightly larger 2θ angles which indicated a relief of intrinsic stress within the films (see Fig. 3(b)).

Statistical analysis was then used to fit the data to a second-order response surface model to find the optimal sputtering conditions. Results indicated that RF power and gas pressure have the largest effects on film crystallization and stress.

4. Conclusions

High quality ZnO films have been deposited by room temperature RF sputtering. ZnO films with large crystallite sizes and minimal surface roughness have been produced. It has been found that increasing RF power and pressure lead to larger crystallite size while increasing O_2 concentration results in smaller sizes. The effect of post-deposition annealing on crystallization and film stress has also been characterized, and annealing has been found to improve the quality of the films while having negligible effect on the surface roughness. The optimal sputtering conditions were: 275 W RF power, 5% O_2 concentration and 1.2 Pa pressure.

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