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Rapid thermal annealing effects on the structural and optical properties of ZnO films deposited on Si substrates

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ABSTRACT

The structural and optical properties of ZnO films deposited on Si substrate following rapid thermal annealing (RTA) have been investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), and photoluminescence (PL) measurements. After RTA treatment, the XRD spectra have shown an effective relaxation of the residual compressive stress, an increase of the intensity and narrowing of the full-width at half-maximum (FWHM) of the (0 0 2) diffraction peak of the as-grown ZnO film. AFM images show roughening of the film surface due to increase of grain size after RTA. The PL spectrum reveals a significant improvement in the UV luminescence of ZnO films following RTA at 800 °C for 1 min.

1. Introduction

Zinc oxide (ZnO) belongs to II–VI compound semiconductor and crystallizes in hexagonal wurtzite structure. At room temperature, ZnO films exhibit very strong emissions by excitons because of the large excitonic binding energy of 60 meV. Furthermore, ZnO has been recognized as a promising photonic material in the UV region due to its wide band gap of 3.37 eV at room temperature [1–7]. So far, various deposition techniques such as sputtering [1,2], molecular beam epitaxy (MBE) [3,4], chemical vapor deposition (CVD) [5,6], and pulsed laser deposition (PLD) [7] have been attempted to grow high-crystalline ZnO films deposited on Si substrates. Among these techniques, the rf magnetron sputtering is the most commonly used technique due to its simple set-up, high deposition rate, and low substrate temperature [1,2].

For depositing high crystal quality ZnO films on Si substrate by rf magnetron sputtering, different deposition conditions such as working pressure, substrate temperature, deposition power, and growth ambient have been considered [1,2]. Unavoidably, the large lattice mismatch and large difference in the thermal expansion coefficients between ZnO films and Si substrates would cause built-in residual stress in the deposited ZnO films [1,8,9]. To improve the crystalline quality of ZnO films grown on Si substrate, the widely known effective technique of thermal annealing treatment can be implemented. There are two kinds of annealing techniques, one is furnace annealing (CFA) and the other is rapid thermal annealing (RTA). Compared to CFA technique, RTA technique offers shorter cycle time, reduced thermal exposure and a lot of size flexibility [10,11]. In view of the advantage of RTA, a study of the controlled details of the RTA parameters for improving the crystal quality of ZnO films should be a subject of great interest. Numerous research works [8,9,12,13] have

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indicated an optimum annealing temperature range of 600–900 °C for effective improvement of the crystallinity of ZnO films. However, there are only few reports on the effects of annealing time on the structural and optical properties of ZnO films [14].

In this work, we study the influence of annealing time on the structural and optical properties of ZnO films by the X-ray diffraction (XRD), atomic force microscopy (AFM), and photoluminescence (PL) techniques. The controlled periods of RTA technique for improving the crystal quality of ZnO films will be studied by analyzing the observed XRD patterns and PL spectra.

2. Experiment

Zinc oxide films were deposited by rf magnetron sputtering system using a ZnO target (99.9%). The substrate is p-type silicon with (1 0 0) orientation. Silicon substrates were thoroughly cleaned with organic solvent and dried before loading in the sputtering system. The chamber was pumped down to 1.5×10^{-5} Torr using a diffusion pump before introducing the premixed Ar and O_2 sputtering gases. Throughout all experiments, the target was presputtered for 15 min under 150 W rf power before the onset of the actual deposition in order to remove any contamination on the target surface, enabling the stabilization and optimal operation of the system. In the actual sputtering process, the sputtering power is controlled at 100 W, the sputtering pressure is 1.33 N/m^2, ratio of O_2/Ar is 0.75, distance between substrate and target is 50 mm, and the substrate is not heated. This procedure was adopted to minimize the effect of different positions in the sputtering system and the sputtering time was 1 h. The thickness of as-grown films was examined by α-step to confirm the uniformity and the film thickness was measured to be around 300 nm. Then the as-grown ZnO sample was divided into six small pieces each with the dimension of 1.0 cm × 1.0 cm. Five of the samples were RTA treated under a constant oxygen flow rate of 500 sccm at 800 °C for 0.5, 1, 3, 5 and 10 min, respectively. During the annealing process, the rising or cooling rate of the temperature was kept at 30 °C/s. The XRD patterns of the ZnO films were obtained using Cu Kα radiation ($\lambda = 1.5405$ Å). AFM (Veeco Digital Instruments Inc.) measurements with tapping mode and 1 Hz scan rate were made on the ZnO thin films to investigate the surface morphologies. The PL measurements were carried out using the 266 nm line with 5 mW power of a microchip laser (Teem Photonics). The laser beam was focused onto a circular spot of size 1 mm diameter to stimulate luminescence. The luminescence was collected using a spectrometer (Jobin Yvon 550) with a 1200 grooves/mm grating and detected using a cooled GaAs photomultiplier tube.

3. Results and discussion

Fig. 1 displays the XRD patterns of the as-grown and the annealed ZnO films following RTA at 800 °C with different annealing time. All samples exhibiting the prominent (0 0 2) diffraction peak indicate the preferential orientation with the c-axis perpendicular to the substrate surface. The (0 0 2) peak position of ZnO films as a function of annealing time is listed in Table 1 and plotted in Fig. 2(a). Since the angular peak position of ZnO powder with (0 0 2) orientation is at $2\theta = 34.43°$ [15], the (0 0 2) peak of the as-grown sample shifting to $2\theta = 34.36°$ indicates the existence of residual stress between the ZnO film and the Si substrate [1,2,8]. Previous reports showed that the residual stresses in ZnO films contain a thermal stress component and an intrinsic stress component [8,9,16]. The thermal stress is due to the difference in the thermal expansion coefficient (α) between ZnO ($\alpha_{11} = 6.05 \times 10^{-6}\,°\mathrm{C}^{-1}$, $\alpha_{33} = 3.53 \times 10^{-6}\,°\mathrm{C}^{-1}$) and silicon substrate ($\alpha = 2.50 \times 10^{-6}\,°\mathrm{C}^{-1}$) [1]. Because the thermal expansion coefficient of ZnO is bigger than that of silicon substrate, the substrate exerts a resultant tensile stress effect to the ZnO film as the substrate cools down from high temperature to room temperature. On the other hand, intrinsic stress has its origin in the imperfection of the crystallites during growth. Several growth parameters, such as deposition temperature, pressure, power, and gas mixture could contribute to the intrinsic stress. In the literature [8,9,16], it has been shown that intrinsic stress of the as-grown ZnO films is compressive. During the growth process, the magnitude of the compressive stress component is larger than that of the thermal (tensile) stress component, therefore the as-grown ZnO films exhibit an overall compressive residual stress.

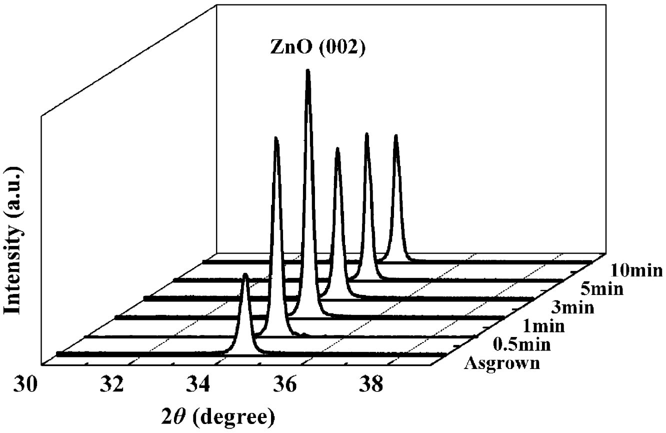

Fig. 1. XRD patterns of the as-grown and the ZnO thin films annealed at 800 °C with different annealing time.

As listed in Table 1, the (0 0 2) peak position of the samples annealed for 0.5 and 1 min locates at $2\theta = 34.41°$ and $34.44°$, respectively. The shift of (0 0 2) peak position toward $2\theta = 34.43°$ indicates that the residual stress in the as-grown ZnO film can be effectively reduced by RTA [8,9,12,13]. With increasing the annealing time over 1 min, the (0 0 2) peak position deviates from the powder value but in the opposite direction, indicating a change in the nature of stress [9,15]. The variation of residual stress would influence the lattice constant "c" of ZnO films. Table 1 also lists the lattice constant of the as-grown and annealed ZnO films obtained from the (0 0 2) reflection in the X-ray line profile. Compared to the strain-free lattice constant ($c_0 = 5.206$ Å) [17], the larger value of the lattice constant in the as-grown ZnO film ($c = 5.215$ Å) shows that the unit cell is elongated along the c-axis and the compressive forces act in the plane of the film [18,19]. By annealing for 0.5 and 1 min, the lattice constant of the annealed ZnO films has decreased to 5.208 and 5.204 Å, respectively. The variation of the lattice constant has clearly shown that the residual stress can be relaxed upon RTA treatment.

The lattice constant can be further utilized to evaluate the average uniform strain, e_{zz} in the lattice along the c-axis [18]:

$$e_{zz} = (c - c_0)/c_0 \tag{1}$$

Further, the biaxial film stress σ is related to the measured c-axis strain by the relation [12,18]

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

where C_{ij} are elastic stiffness constants. For ZnO, we have $C_{13} = 106.1$ GPa, $C_{11} = 207.0$ GPa, $C_{12} = 117.7$ GPa, and $C_{33} = 209.5$ GPa [20]. The biaxial stresses for the as-grown and the annealed ZnO films have been derived from Eq. (2) and presented in Table 1 and Fig. 2(b). Obviously, the residual stress of the as-grown ZnO film is compressive. By annealing at 800 °C for 0.5–1 min, the