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Effects of RTA-treated ZnO/Quartz Thin Films on the Structural and Optical Properties

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ZnO thin films have been successfully grown on the quartz substrate by RF magnetron sputtering technique. The effects of rapid thermal annealing (RTA) on the structural and optical properties has been investigated by means of X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL) measurements. The structural defects of ZnO thin films were reduced during the RTA processes and the crystallinity was improved after the RTA treatments. It is also found out that RTA treatments can remarkably improve the ZnO crystallinity and enhance the UV emission in the wavelength range of 335 – 450 nm over the annealing temperature range of 600 – 800 °C.

1. Introduction

Zinc oxide (ZnO) is a wide-band-gap (3.37 eV) semiconductor at room temperature and has a low threshold for optical pumping, a large exciton binding energy of 60 meV, the availability of a ZnO substrate, wet chemical processing is possible, more resistant to radiation damage, and the possibility of high doping (1). These exclusive characteristics make ZnO over its main competitor, gallium nitride (GaN) and very useful in the applications to the efficient short-wavelength optoelectronic devices, such as ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs) for the light sources of high-density optical recording or medical equipment (1). In addition, besides the earlier-mentioned optical and chemical properties, the ZnO is piezoelectric, transparent in the visible, and can be made conducting with appropriate dopants (2). Therefore, it is possible to find other wide applications in optic-electric integration. In recent years, some techniques have been used to synthesize high quality ZnO thin films such as metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and RF magnetron sputtering (3-6). Moreover, it is reported that the physical properties of ZnO thin films are strongly related to the technology of the deposition and the conditions of the growth process as well as of the post-annealing process (7-9). Despite the progress in the improvement of ZnO layers, there are not many reports on the influence of structural and optical properties of ZnO thin films grown on the quartz substrates treated by using a rapid thermal annealing (RTA) method (10,11).

In this work, we report the fabrication of ZnO thin films by using RF sputtering technique on the quartz substrates. The as-deposited ZnO/Quartz films were treated under RTA method at different selected temperatures in N_2 gas ambient, enabling us to investigate the changes in structural and optical properties with RTA treatments.

2. Experimental

ZnO thin films were grown by RF magnetron sputtering system equipped with a ZnO target with purity of 99.9%. Quartz was used as a substrate. The quartz substrates were degreased with organic solutions in an ultrasonic bath and dried before loading in the sputtering system. The sputtering chamber was evacuated to 1.5×10^{-5} torr using a diffusion pump before introducing the pre-mixed O_2 (oxygen) and Ar (argon) sputtering gases. Prior to deposition, the targets were pre-sputtered for 15 minutes under an RF power of 150 W in order to remove any contamination on the target surface and make the system stable and optimum condition. The sputtering was carried out in the ambient with O_2/Ar ratio of 0.75 at a constant sputtering pressure of 1.33 N/m^2, sputtering power of 100 W and substrate is not heated with a target-to-substrate distance of 5 cm. Four pieces of ZnO samples were cut from the as-deposited ZnO sample. Three ZnO samples were treated under RTA method at different selected temperatures (400, 600 and 800 °C, respectively) in nitrogen (N_2) ambient for 30 sec, and one ZnO sample received no RTA treatment. During the annealing process, the ramping rate of the temperature was kept at 25 °C/s. The crystallinity, the surface morphology, and the optical properties of the as-deposited and RTA-treated ZnO films were examined by X-ray diffraction (XRD) using a Rigaku RTP 300RC X-ray diffractometer with Cu Kα as the line source (λ = 1.542 Å), atomic force microscopy (AFM; Veeco Digital Instruments, Inc.), photoluminescence (PL) spectroscopy using a laser (λ = 266 nm) with a power density of 5 mW/cm^2 as an excitation source was used to study the optical properties in the wavelength range of 335 – 450 nm.

3. Results and discussion

Figure 1 shows the θ–2θ XRD spectra of the as-deposited and RTA-treated ZnO thin films in the range of 33 – 36°. The XRD patterns for the as-deposited and all the RTA-treated films showed a single strong ZnO (002) peak at around 34.4°, The presence of the dominant (002) diffraction peak indicates that the ZnO films have a well defined crystal orientation (hexagonal wurtzite structure), where the *c*-axis direction is perpendicular to the substrate plane (12). Meanwhile, the improvement has been made on the full-width at half-maximum (FWHM) of the RTA-treated samples and the value is about 0.19° at 600 and 800 °C. Therefore, the RTA film is more oriented than the as-deposited film and is also quite similar to the previous work presenting the high crystal quality (13). The crystallite sizes of the ZnO films can be evaluated from the value of FWHM of the (002) diffraction peak by the Scherrer equation: $D = 0.94 / \beta\cos\theta$, where λ (1.542 Å) is the X-ray wavelength and β is the FWHM in radians (14). The average crystallite size is a measure of crystallinity and is therefore related to the average grain diameter. Our estimated values are in the range of 35 – 50 nm and slight increase with increasing RTA temperatures. From the results of XRD, it is indicated that the structural defects of ZnO thin films were reduced during the RTA processes and the crystallinity was improved after the RTA treatments.

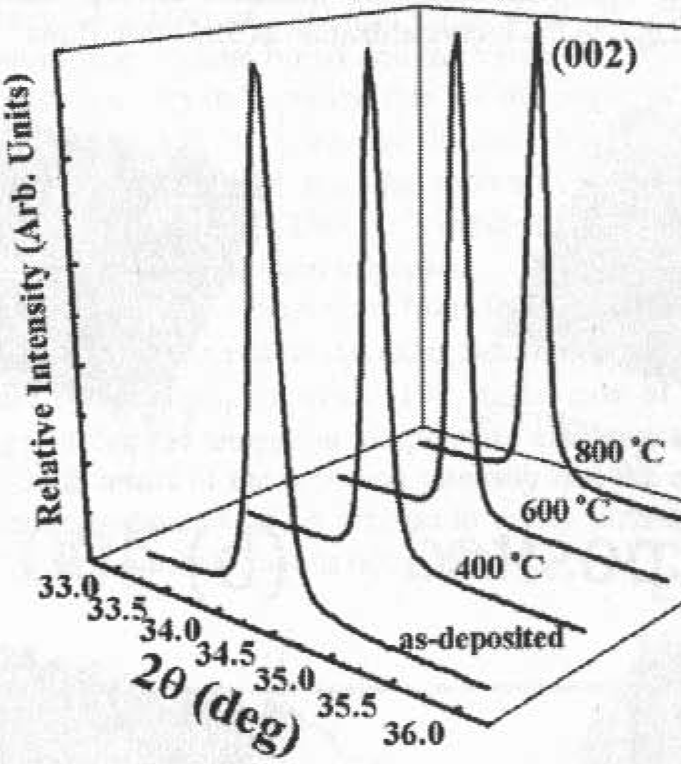
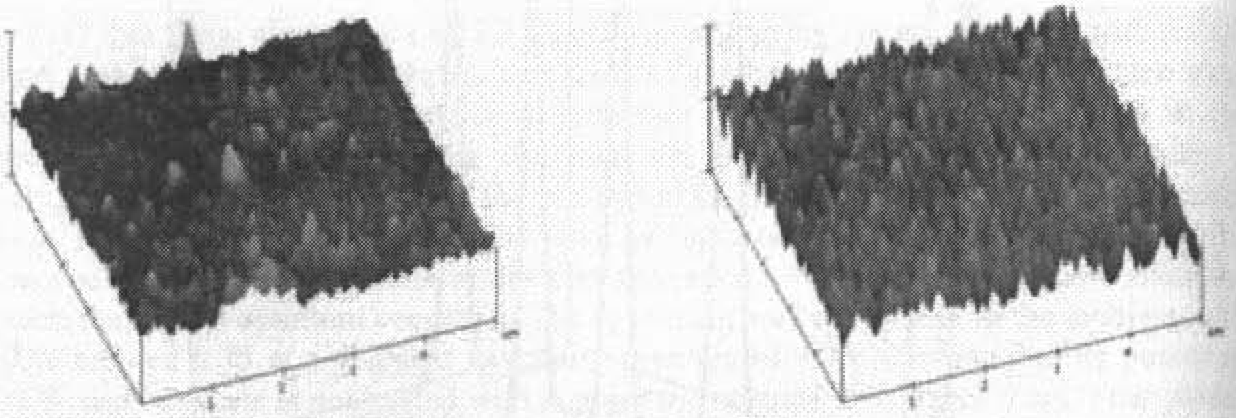
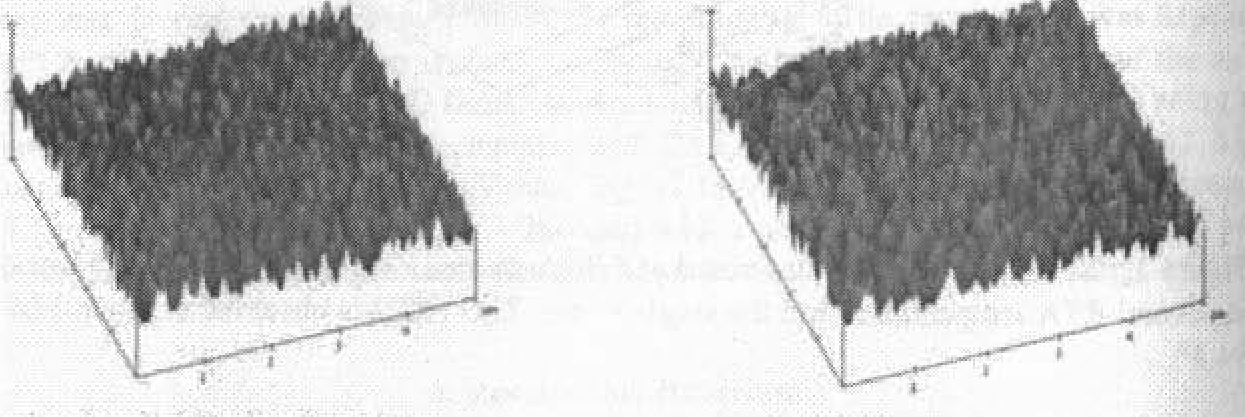


Figure 1. XRD patterns of as-deposited and RTA-treated ZnO films on quartz substrates at several RTA temperatures and the single strong ZnO (002) is observed at around 2θ = 34.4°.

In order to investigate the changes in surface morphology as a function of RTA temperature, ZnO film surface areas were measured with AFM measurements. Figure 2 shows the surface morphology variations of ZnO thin films over a scale of 5 μm×5 μm from the observed AFM images at several RTA temperatures. It is shown that the film was deposited in a column-by-column growth process and the grain size became larger with the augments of RTA temperature. AFM analysis of RTA-treated ZnO films under different RTA temperatures shows that the particle size in the film treated under 400 °C is 100 – 120 nm and those films treated at 600 °C and 800 °C are 130 – 150 nm. Fang et al. indicated that the particle size of ZnO films analyzed by AFM is much larger than that by XRD and also suggested that AFM gives the particle size, while XRD gives the grain size (15). This also agrees with the results shown in XRD which is confirmed that RTA treatment does not change the spread in orientations of the grains giving rise to (002) diffraction peaks, so grain growth alone must be responsible for the changes in (002) peak widths. Additionally, the mean roughness (R_a) of as-deposited film is about 6 nm, while R_a is around 13 nm for all of the RTA-treated samples. The increase in the roughness may be due to the growth and integration of the major grains. On the other hand, the better roughness is always required for the most optoelectronic applications. Fujimura et al. suggested that the surface energy density of the (002) orientation is the lowest in the ZnO crystal (16). At high temperature, the atoms have enough diffuse activation energy to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger at high temperature. Then the growth orientation develops into one crystallographic direction of the low surface energy, leading to the improvement of ZnO crystallinity. Therefore, it can be described that the RTA process in N_2 ambient is an effective way for supplying sufficient thermal energy to improve the quality of ZnO thin film due to the recrystallization of ZnO thin films.



(a) as-deposited (b) 400 °C



(c) 600 °C (d) 800 °C

Figure 2. Surface morphology variations of as-deposited and RTA-treated ZnO thin films from the observed AFM images.

Optical properties were investigated from the PL spectra. In general, it has been believed that the visible emission of ZnO film has a relation with impurities or point defects in the film (6,17). Figure 3 shows the room temperature PL spectra of the as-deposited and RTA-treated ZnO thin films at various temperatures in the wavelength range of 335 – 450 nm. These spectra are characterized by the observed PL emission in the UV wavelengths, peaking at around 370 – 380 nm (3.26 – 3.35 eV). Apparently, our results are in agreement with one of the major PL peaks as mentioned in the previous reports that ZnO material displays a strong UV near-band-edge (NBE) emission at around 380 nm (3.26 eV) because of an exciton-related activity (1,9,12). Due to the large exciton binding energy of ZnO (~ 60 meV), excitons have been observed at room temperature. It has also been reported that thermal energy at room temperature can break the bound excitons into free excitons due to the small binding energy of bound excitons (18). The UV emissions are all observed for the as-deposited and RTA-treated ZnO thin films which are assignable to the exciton transition bound to neutral donor. However, considerable change was not observed except a little increase of the lineshape of the PL UV emission was enhanced and getting sharper as the RTA temperature increases, which is related to the structural defects of ZnO thin films. In the PL spectrum of as-deposited film, the UV emission band is quite broad and the value of FWHM is around 400 meV. Therefore, the shows poor crystal quality due to the intrinsic defects. As the RTA temperature increases up to 600 °C, emission intensity became better and the value of FWHM of emission is about 200 meV. It is also shown that the PL spectrum of 800 °C is similar to the PL spectrum of 600 °C. Thus, it is evident that the luminescence properties of RTA-treated ZnO thin films have been improved.

Comparing to the annealing temperature from the previous literatures, the best PL properties of ZnO thin films prepared by annealing technique are reported to be 800°C by Hong et al. (11) and 900 °C by Chen et al. (19). In the case of our RTA treatments in nitrogen ambient reveal that the annealing temperature increases as above 600 °C, crystal quality was improved in terms of the emission intensity and the emission FWHM. It can be suggested that the importance of RTA process to obtain high-quality ZnO thin films is at the optimum RTA temperature of about 600 – 800 °C.

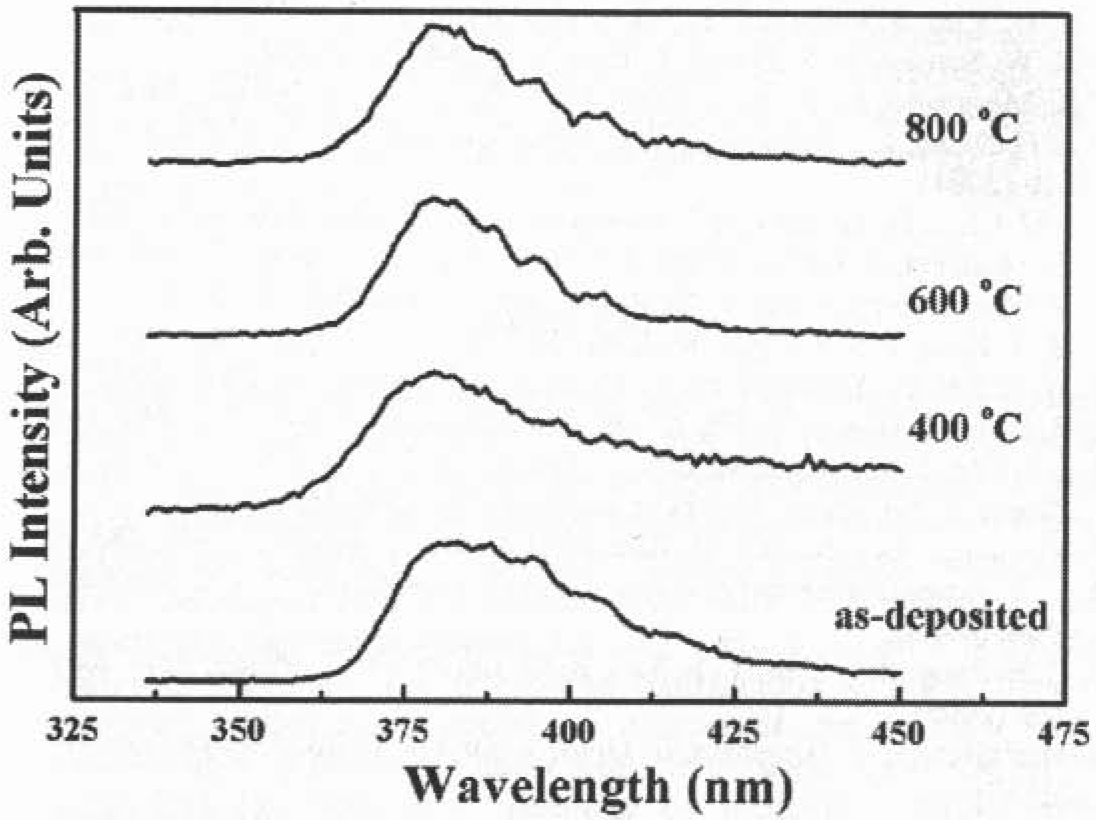


Figure 3. PL spectra of the as-deposited and RTA-treated ZnO thin films over the wavelength range of 335 – 450 nm at room temperature.

4. Conclusions

Various effects of RTA treatments on the structural and optical properties of sputtered ZnO thin films have been studied. X-ray diffraction and room temperature PL studies showed that RTA-treated ZnO films exhibited a high structural quality and a good UV emission. From our investigations, the optimum RTA temperature was found to be in the range of 600 – 800 °C. Considerable variation of surface morphology was not observed; however, the grain size becomes larger at the RTA temperature of 600 and 800 °C, which might be corresponding to the PL and XRD observations. The improvement of crystal quality of ZnO thin films grown on quartz-substrate, RTA at higher temperature is primarily required to supply sufficient thermal energy for the recrystallization. Moreover, the appropriate control of RTA temperature is also needed not only to diminish the structural defects but also to improve the crystalline quality.

Acknowledgments

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