The structural and optical properties of ZnO/Si thin films by RTA treatments

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Abstract

ZnO/Si thin films were prepared by rf magnetron sputtering method and some of the samples were treated by rapid thermal annealing (RTA) process at different temperatures ranging from 400 to 800 °C. The effects of RTA treatment on the structural properties were studied by using X-ray diffraction and atomic force microscopy while optical properties were studied by the photoluminescence measurements. It is observed that the ZnO film annealed at 600 °C reveals the strongest UV emission intensity and narrowest full width at half maximum among the temperature ranges studied. The enhanced UV emission from the film annealed at 600 °C is attributed to the improved crystalline quality of ZnO film due to the effective relaxation of residual compressive stress and achieving maximum grain size.

1. Introduction

ZnO (zinc oxide) belongs to the family of II–VI compound wide-gap semiconductor with a room temperature direct band gap of 3.37 eV and a large exciton binding energy of about 60 meV, which makes it a very attractive material for the applications to the advanced optoelectronic devices [1,2]. So far, many different growth techniques such as sputtering, pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) have been used on the production of ZnO thin films [3–6]. However, the crystal quality of ZnO thin films strongly depends on the growth techniques, growth conditions and selected substrates. Numerous researchers have attempted to grow high crystalline ZnO films deposited on Si substrates because of the lower cost and larger wafer size [7]. Moreover, the large lattice mismatch and large difference in the thermal expansion coefficients between ZnO films and Si substrates have resulted in a built-in residual stress to exist in the deposited ZnO films. Therefore, it is a challenge to obtain better crystal quality of ZnO thin films deposited on Si substrates (ZnO/Si). Among the different deposition techniques, rf sputtering is the most commonly used technique due to its simple set-up, high deposition rate and low substrate temperature. However, in order to produce high quality of ZnO/Si films by rf sputtering technique, it is necessary to have an optimal control of deposition conditions such as working pressure, substrate temperature, deposition power and growth ambient [2,3]. On the other hand, the temperature annealing treatment is widely known as a conventional and an effective technique to improve the crystalline quality. Hong et al. [8] and Jung et al. [9] have studied the effects of annealing on the characteristics of

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sputtered ZnO/Si films and showed that higher annealing temperature can effectively improve crystallinity. However, it takes a rather long time at high temperature for conventional furnace annealing (CFA) to have the effects on film stress, film microstructure and film surface layers. An alternative technique is rapid thermal annealing (RTA). The merit of RTA method is the simplicity of the process. RTA offers short cycle time, reduced thermal exposure and lot size flexibility compared to CFA process. By contrast, this technique requires a high temperature, but the annealing time is only a few seconds [10–14]. We can modulate the structural and optical properties of ZnO/Si films by controlling the RTA treatment conditions in a short time.

In this work, we present the structural and optical properties of ZnO/Si thin films treated by the RTA method under nitrogen ambient at different selected temperatures. The relationship between the quality of the ZnO thin films and the RTA temperatures is also studied by the XRD and PL spectra.

2. Experimental procedures

ZnO thin films were grown by rf magnetron sputtering system equipped with a ZnO target with the purity of 99.9%. The p-type silicon with (1 0 0) orientation was used as a substrate, and it was thoroughly cleaned with organic solvents 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 min under an rf power of 150 W in order to remove any contamination on the target surface. 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 was not heated with a target-to-substrate distance of 5 cm. Sputtering time was 1 h and the film thickness was measured to be around 500 nm by a surface profiler. Four pieces of ZnO samples were cut from the as-deposited ZnO sample. Three ZnO samples were transferred to the RTA chamber (HPC-7000, ULVAC) and treated at different selected temperatures (400, 600 and 800 °C, respectively) in nitrogen (N_2) ambient with a purity of 99.995% for 30 s and one ZnO sample received no RTA treatment. During the annealing process, the rising or cooling rate of the temperature was kept at 30 °C/s.

The crystal structure dependence on the RTA treatment was characterized by X-ray diffraction (XRD) using a Rigaku RTP 300RC X-ray diffractometer with Cu Kα as the line source ($\lambda = 1.542$ Å). Atomic force microscopy (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. Photoluminescence (PL) measurements at room and low temperatures were carried out utilizing a 266 nm UV line of the microchip laser (Teem Photonics) to study the optical properties in the wavelength range of 345–425 nm. The excitation intensity of the laser was 5 mW/cm^2. 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 shows the XRD patterns of the as-deposited and RTA-treated ZnO thin films in the 2Θ (degree) range of 33–36° at different annealing temperatures. As can be seen from the XRD patterns, the (0 0 2) diffraction peaks characterize the hexagonal wurtzite structure showing the prominent *c*-axis oriented [15]. It is also found that the diffraction peak of the as-deposited film is relatively weak and broad at around 34.18°. The estimated peak position of RTA temperatures at 400, 600 and 800 °C are 34.31°, 34.38° and 34.38°, respectively. Comparing to the as-deposited sample, the diffraction angle shifts toward the reference strain-free ZnO film (34.40°) with the increase in the RTA temperature showing the relaxation of the existing residual compressive stress between ZnO and the Si substrate [11]. Therefore, these results indicate the residual compressive stress can be relaxed effectively by the RTA process [2,3,11]. The fitted values of full-width at half maximum (FWHM) of (0 0 2) peak of the as-deposited and RTA-treated ZnO/Si films are also listed in Table 1. The FWHM for the as-deposited sample was fitted to be 0.199° and decreased significantly to 0.170° for the sample annealed at 600 °C.

The origin of the residual stress in the as-deposited ZnO/Si film can also be realized as the followings: it is known that the residual stress in ZnO films contains a thermal stress component and an intrinsic stress component [2]. The thermal stress is due to the difference in the thermal expansion
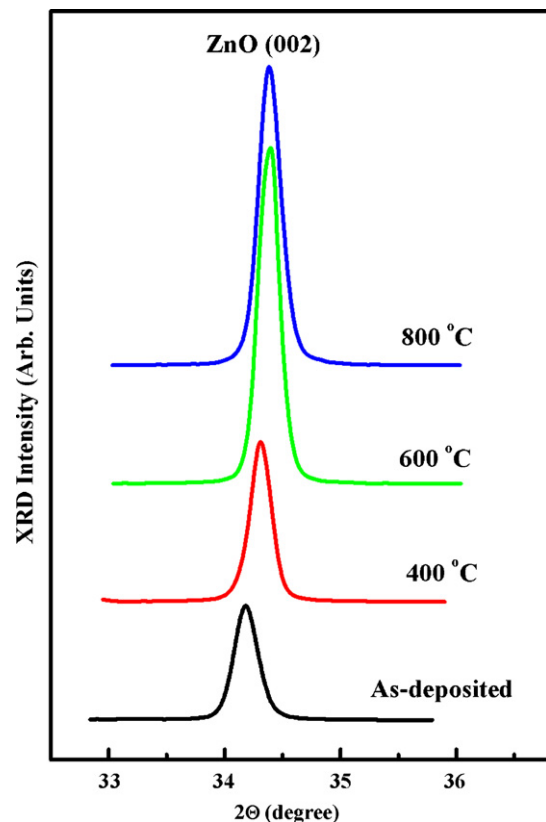

Fig. 1. XRD patterns of the as-deposited and RTA-treated ZnO thin films in the 2Θ (degree) range of 33–36° at different annealing temperatures.

Table 1
Some estimated parameters for the structural and optical properties from the XRD and PL measurements of ZnO/Si thin films at different selected RTA temperatures

RTA temperature	XRD		PL	
	2Θ angle (degree)	FWHM (degree)	12 K FWHM (meV)	300 K FWHM (meV)
As-deposited	34.18 ± 0.01	0.199 ± 0.002	84 ± 1.5	105 ± 2.1
400 °C	34.31 ± 0.01	0.183 ± 0.002	76 ± 1.5	101 ± 2.1
600 °C	34.38 ± 0.01	0.170 ± 0.001	67 ± 1.2	89 ± 1.8
800 °C	34.38 ± 0.01	0.172 ± 0.001	71 ± 1.2	92 ± 1.8

coefficient between ZnO $(4.75 \times 10^{-6}\,\text{K}^{-1})$ and silicon substrate $(2.6 \times 10^{-6}\,\text{K}^{-1})$ [16]. Since the thermal expansion coefficient of ZnO is larger than that of the silicon substrate, the substrate exerts a resultant tensile stress on the ZnO film 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 growth parameters, such as deposition temperature, deposition pressure, deposition power and gas mixture would contribute to the intrinsic stress. The intrinsic stress in ZnO should be compressive and its magnitude is larger than the (tensile) thermal stress component, resulting in an overall residual compressive stress in the as-deposited ZnO films [2].

The average grain sizes of the films can be calculated from the value of FWHM of the (0 0 2) diffraction peak by the Scherrer's equation: $D \approx 0.9\lambda / \beta \cos \Theta$, where λ is the X-ray wavelength and β is the value of FWHM in radians [17]. Our estimated values of the as-deposited and RTA-treated samples at 400, 600 and 800 °C are 42, 45, 49 and 48 nm, respectively.

Thus, the XRD analysis indicated that the RTA-treated ZnO film at 600 °C resulted in the largest average grain size with the narrowest FWHM and good c-axis orientation.

Fig. 2(a)–(d) shows the surface morphology variations of the ZnO thin films over a scale of 5 μm × 5 μm from the observed AFM images at different RTA temperatures. Upon inspection of the images in the AFM measuring system, it is observed that the grain sizes become larger with the augments of the RTA temperatures and the grain size for the as-deposited sample is around 121 nm. For the RTA-treated sample the grain sizes are in the range of 187–192 nm and are comparable to the largest grain size of 200 nm from the previous reported data [18]. The root-mean-square (RMS) is in the range of 15–20 nm. In comparison, the grain size of ZnO films analyzed by AFM is much larger than that by XRD. This difference is probably because the grain size measured from AFM is the surface morphology of coalesced grains which gives the particle size [18]. In addition, Lin et al. suggested that a temperature can stimulate the migration of grain boundaries and cause the
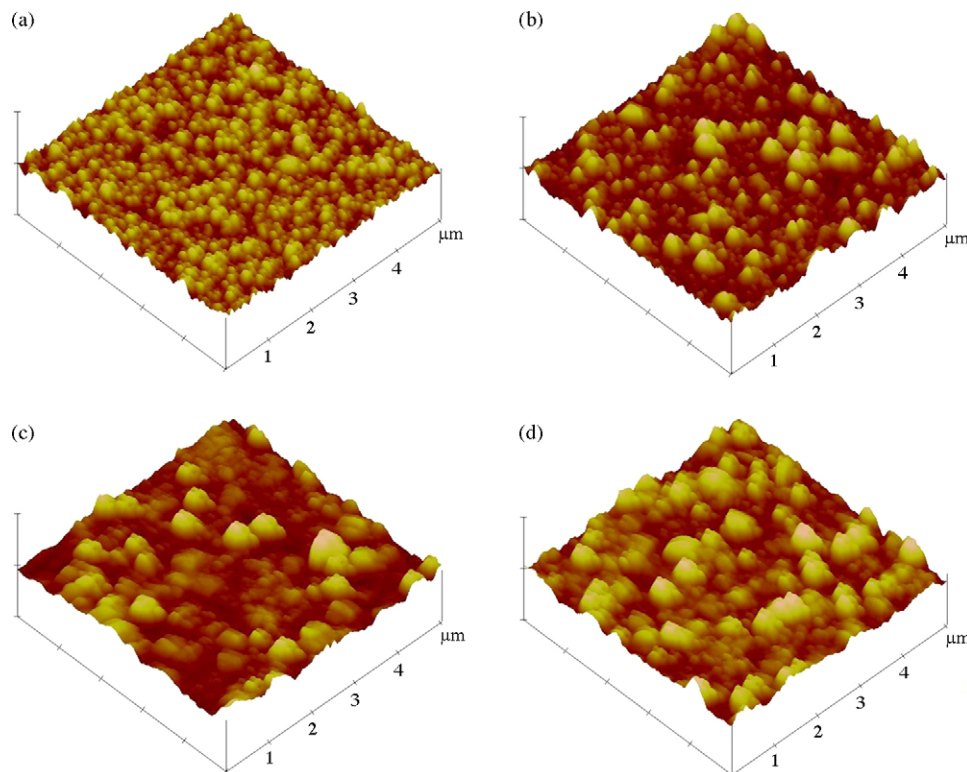

Fig. 2. Surface morphology variations of ZnO thin films from the observed AFM images: (a) as-deposited, (b) RTA-treated at 400 °C, (c) RTA-treated at 600 °C and (d) RTA-treated at 800 °C.
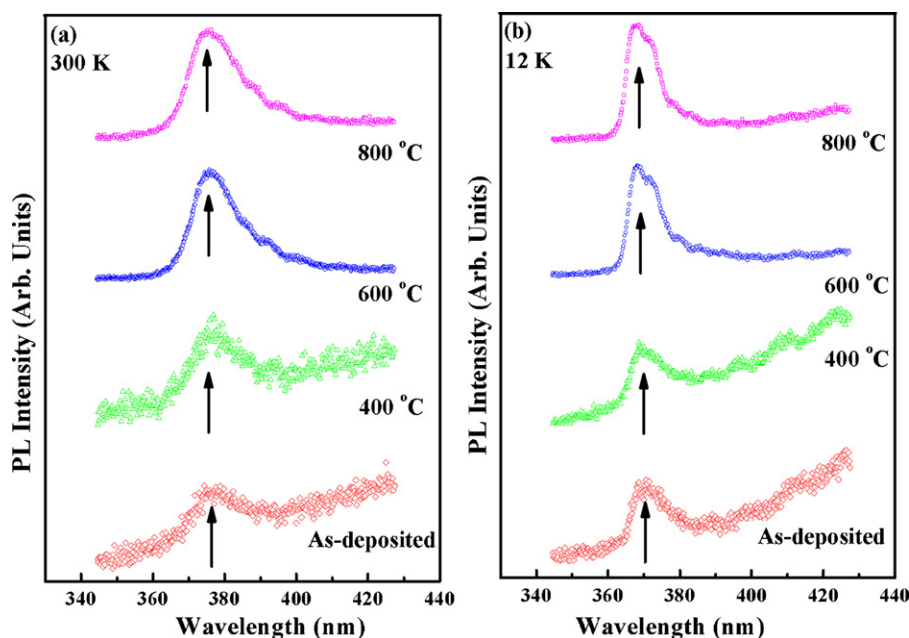
Fig. 3. PL spectra of the as-deposited and RTA-treated ZnO thin films over the wavelength range of 345–425 nm at 300 and 12 K, respectively.

coalescence of more grains during annealing processes [14]. This also agrees with the results shown in XRD which confirms that RTA treatment does not change the spread in orientations of the grains giving rise to (0 0 2) diffraction peaks, so grain growth alone should be responsible for the changes in (0 0 2) peak widths [19]. Furthermore, there is marked difference between microstructure of the thin film after RTA. Fujimura et al. described that the surface energy density of the (0 0 2) orientation is the lowest in the ZnO crystal [20]. At high temperature, the atoms have sufficient 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 [19]. Then the growth orientation develops into one crystallographic direction of the low surface energy, leading to the increases of ZnO grain sizes.

As a potential photonic material, it is important to evaluate the optical properties of ZnO/Si thin films. Fig. 3(a) and (b) displays the PL spectra of the as-deposited and RTA-treated ZnO thin films over the wavelength range of 345–425 nm at the temperature of 300 K and a low temperature of 12 K, respectively. For clarity, all spectra in Fig. 3 were normalized. The PL emission in the UV bands was observed, peaking at the range of 370–380 nm (indicated by the arrow signs) and is consistent with the results reported in the previous literatures that ZnO material displays a strong UV band assigned to the near-band-edge (NBE) emission at around 380 nm, [11,15]. As shown in Fig. 3, the PL properties seem to be improved with increases in RTA temperatures and the lineshapes of the UV band emissions became narrower which are related to the crystal quality of ZnO thin films [21]. Although all the UV emissions are observed for the as-deposited and RTA-treated ZnO thin films, the weak deep-level-emission (DLE) tails can only be defined for the as-deposited and the RTA-treated sample at 400 °C. Wang et al. indicated that the origin of DLE band is attributed to several intrinsic defects such as oxygen

vacancy (V_o) and zinc interstitial (I_{Zn}) which are responsible for the suppression of the DLE [22].

Among the PL results at 300 K, the estimated values of FWHM of the PL spectra for as-deposited and RTA-treated samples at 400, 600 and 800 °C are 105, 101, 89 and 92 meV, respectively. It is observed that the optical properties of ZnO films have been improved with the increases of RTA temperature and the ZnO films annealed at 600 °C reveals the strongest UV emission intensity and the narrowest FWHM of the temperatures investigated. Depending on the various annealing parameters for ZnO/Si films, the optimum annealing temperature has been reported at 800 °C by Jung et al. [9] and 410 °C by Wang et al. [22], respectively. In this work, we observe that the optimum temperature is at 600 °C. However, the crystal quality of ZnO/Si film might be degenerated at the annealing temperature of 800 °C. This
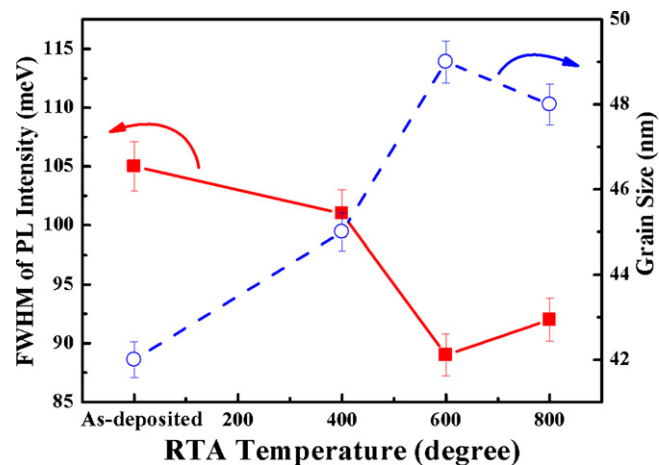

Fig. 4. The FWHM of PL intensity at 300 K (closed squares with solid line) and the grain sizes from XRD patterns (open circles with dashed line) for the ZnO films as a function of RTA temperatures.

discrepancy could be related to both recrystallization and interdiffusion between ZnO layer and Si substrate during the higher annealing temperature [9]. The rest estimated values of FWHM from the PL spectra at 300 and 12 K, respectively are also listed in Table 1.

With the increase of RTA temperatures, the orientation of the ZnO films, as well as the grain size, is improved. The PL spectra show an identical trend compared to the XRD results as both crystallinity and optical properties were simultaneously improved. Fig. 4 shows the FWHM of PL emission line at 300 K (closed squares with solid line) and grain sizes from XRD patterns (open circles with dashed line) as a function of RTA temperatures. Kim et al. suggested that due to sufficient thermal energy supplied by increase of the growth temperature, atoms moved to stable sites and those impurities moved to grain boundary [23]. Thus, it is evident that the improvement of PL properties in this experiment can be explained in terms of the grain size increase [23].

4. Conclusions

The results demonstrate that rf magnetron sputtering technique combined with RTA process can be implemented for the improvements of the structural and optical properties of ZnO/Si thin films. From our investigations, the optimum RTA temperature was found to be at 600 °C for the effective relaxation of residual compressive stress and achieving maximum grain size for the ZnO samples. The narrow PL linewidth is regarded as a clear evidence of crystal quality improvement. Microstructure at the ZnO/Si interface is effectively changed by RTA treatments. Moreover, the RTA method turns out to have the ability to reduce structural defects and enhance the UV emission in the wavelength range of 370–380 nm.

Acknowledgements

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