Optical properties of ZnO thin films on SiO_2 substrates deposited by radio frequency magnetron sputtering

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The optical properties of both the annealed and as-deposited ZnO thin films by radio frequency (RF) magnetron sputtering on SiO_2 substrates were studied. In the annealed films, two pronounced well defined exciton absorption peaks for the A and B excitons were obtained in the absorption spectra, a strong free exciton emission without deep-level emissions was observed in the photoluminescence (PL) spectra at room temperature. It was found that annealing the films in oxygen dramatically improved the optical properties and the quality of the films.

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Zinc oxide (ZnO) is a wide direct-gap semiconductor of wurtzite structure. It has a band gap of 3.37 eV at room temperature (RT) which is in the ultraviolet (UV) range, its exciton binding energy (60 meV) is much larger than the RT ionized energy (26 meV), which permits excitonic recombination well above RT. Research groups have demonstrated room UV lasing from ZnO films grown on sapphire[1−3], this makes it possible to fabricate ZnO-based UV light emitting devices. In addition, ZnO has large excitonic laser gain, low optical loss and low power threshold for optical pumping at RT[4,5], these properties make it among the most promising materials for blue and UV laser diodes (LDs) and light emitting diodes (LEDs) in the near future.

To date the ZnO thin films have been grown by metal organic chemical vapor deposition (MOCVD)[6], plasma-assisted molecule beam epitaxy (P-MBE)[7], and pulsed laser deposition (PLD)[8] on sapphire. However, there are no reports on high quality ZnO thin films deposited on SiO_2 by radio frequency (RF) sputtering. In this paper, optical properties of ZnO thin films deposited on SiO_2 by RF sputtering were investigated. X-ray diffraction (XRD), absorption and photoluminescence (PL) measurements were employed to study the crystal structure and optical properties of the films, the results show that high quality ZnO thin films have been successfully deposited on SiO_2 by RF sputtering with optimized deposition and annealing conditions. Post-annealing in oxygen takes an important role in forming high quality ZnO and enhancing the optical properties of the deposited films.

The ZnO films used in this study were deposited by RF magnetron sputtering on SiO_2 substrates. The ratio of Ar to O_2 was about 7 : 2 with 3-mTorr gas pressure, the substrate temperature was about 230 °C, the post-annealing temperature was 550 °C and the process lasted 1.5 hour.

The crystal structure was then characterized by XRD using CuK_a ($\lambda = 0.15405$ nm) radiation. Figure 1 shows the XRD spectra of both the as-deposited and the annealed ZnO thin films prepared by RF sputtering. For the annealed sample there is a sharp ZnO (0002) peak at $2\theta = 34.48°$, which yields a d spacing of 0.2599 nm, while the ZnO (0004) peak at 72.87° can hardly be seen. From the XRD θ-2θ scan, we can get the lattice constant of $c = 2d = 0.5198$ nm, well in agreement with the bulk ZnO ($c = 5.207$ nm)[7]. For this sample, the full width at half maximum (FWHM) is only 0.18°, compared with 0.20° FWHM of the ZnO films on Si substrates grown by plasma enhanced chemical vapor deposition (PECVD)[9], its small XRD FWHM suggests that the annealed film has a highly c-axis preferred orientation. The mean crystallite size d can be calculated from the (0002) diffraction peak width using Sherrer's formula[10]

$$d = 0.94/\Delta(2\theta) \cdot \lambda/\cos(\theta),$$

where λ is the X-ray wavelength, θ is the diffraction angle (17.24°), $\Delta(2\theta)$ is the line width at half maximum, then we get the mean grain size of 50 nm for this sample.

The XRD spectrum of the as-deposited sample is shown in Fig. 1(b), it also has a sharp ZnO (0002) peak, but the FWHM of the XRD peak is much broader than the annealed one, which is 0.39° at $2\theta = 33.91°$, at the same time, the diffraction intensity decreases greatly.

Compared with the as-deposited sample, the much smaller FWHM and stronger intensity of XRD peak of the annealed one indicate annealing can greatly improve the c-axis preferred orientation of the ZnO film and its crystallinity, in addition, annealing gets the position of XRD peak further near to that of the ZnO single crystal.

The absorption spectra at RT for both the annealed and as-deposited samples are shown in Fig. 2. For the as-deposited sample, there is a broadened free exciton absorption peak lying in 3.400 eV. However, for the annealed sample two distinct absorption peaks can be seen in the near band edge, individually labeled in order of the valence as A and B, lying in 3.338 and 3.394 eV. There is a slight energy shift and a distinct increase in the sharpness of the rise in the absorption coefficient in near band edge range with annealing, these characteristics for the annealed ZnO films via the as-deposited films on SiO_2 are the same as that of ZnO thin film grown on some other substrates[11]. The result of the slight energy lowering of

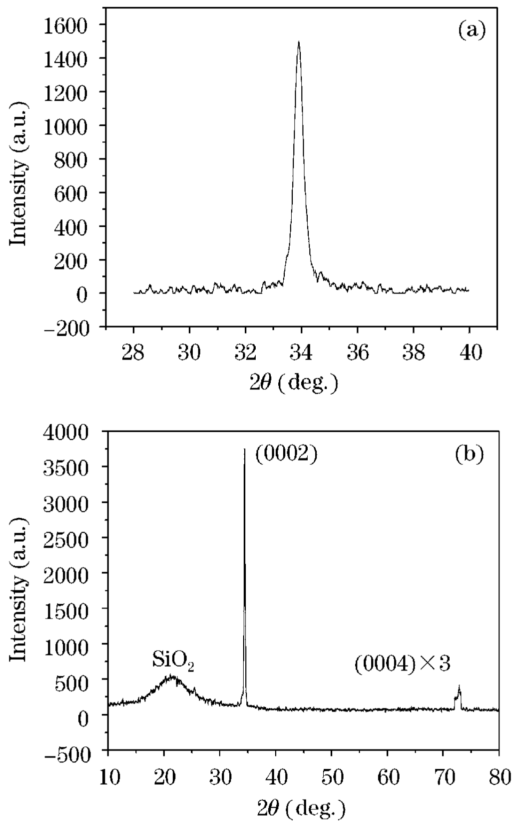

Fig. 1. XRD θ-2θ scan of ZnO films as-deposited (a) and annealed (b) in oxygen at 550 °C for 1.5 hour.

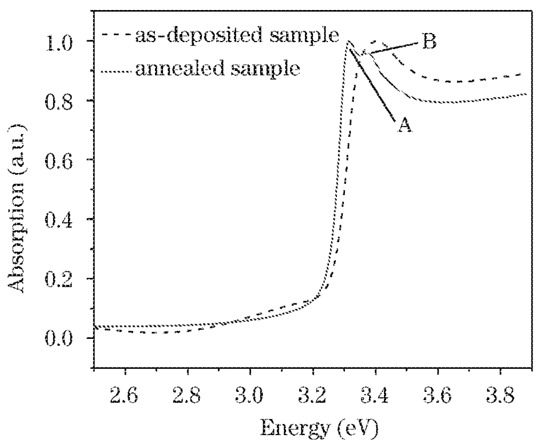

Fig. 2. Absorption spectra and excitonic structure for the as-deposited and annealed ZnO films measured at RT.

the absorption edge might be that annealing the crystal relieved the strain slightly[11].

It is worthily noted that the spectral shape of the peaks in the absorption spectra for the annealed sample is well coincided with the exciton absorption spectra of ZnO single crystal epitaxial films[12]. The Coulomibc interaction on the absorption spectrum is very different to the square root dependence expected for independent electronics and holes. With the theoretical Wannier-Mott exciton model and Reynolds' works[13], the following scheme is for the exciton spectrum in the ZnO crystal: the lowest conduction band $\Gamma 7$ and valence bands $\Gamma 9$, $\Gamma 7$, and $\Gamma 7$ form three exciton series A ($\Gamma 7\times\Gamma 9$), B ($\Gamma 7\times\Gamma 7$) and C ($\Gamma 7\times\Gamma 7$). This imposes selection rules for optical transitions, such that the A and B excitons should have oscillator strength for $E\perp c$ polarization and $E \parallel c$ polarization is necessary for the C exciton. Therefore, since incident light is normal to the sample and the film has a highly c-axis preferred orientation normal to the substrate, the A and B exciton transitions are allowed and C exciton transition is forbidden, which may be interpreted as the situation that only A and B without C exciton absorption peaks appear in the absorption spectrum of the annealed ZnO film in Fig. 2.

Excitons provide a sensitive indicator of material quality. Mechanisms that broaden or shift the exciton resonance such as defect, strain, phonon interactions in turn broaden and shift the absorption edge. The presence of A, B excitons and the sharpness of the absorption edge indicate high quality of our annealed samples with little defects, and post-annealing has greatly improved the crystalinity of the deposited films.

The RT PL spectra are shown in Fig. 3, the 325-nm line of a continuous wave He-Cd Laser was used as the excitation source. For the as-deposited sample in Fig. 3(a), it has a broadened FWHM of the emission peak compared with the annealed film, which are the overlapped emissions of free exciton and defect recombination. By analogy with GaN[7], the broadened emission might be the result of transitions involving oxygen vacancy V_O, interstitial zinc Zn_i, and antisite defect O_{Zn}. Annealing in oxygen can greatly reduce the concentrations of these kinds of defects, so as to improve the

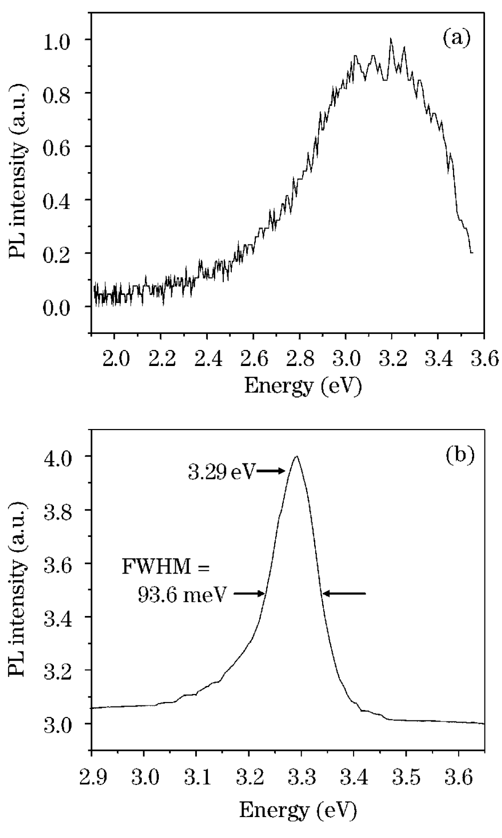

Fig. 3. PL spectra for the as-deposited (a) and annealed (b) ZnO films measured at RT.

as-deposited ZnO crystallinty, just as that can be seen from the PL spectrum of the annealed sample in Fig. 3(b), a sharp single free-exciton emission dominates the spectrum at 3.29 eV with a FWHM of 93.6 meV, compared with the 117 meV observed for MBE-grown ZnO thin films at RT[7], meanwhile, there are no deep level emissions. In Ref. [14], the films grown on glass substrates by RF magnetron were reported, compared with their appearance of deep level PL emissions under different excitation wavelength, the optical properties and quality of our annealed sample are shown to be better.

In conclusion, absorption measurement and PL were used to investigate the optical properties of ZnO thin films deposited by RF sputtering. It was found that the post-annealing in oxygen at 550 °C for 1.5 hour dramatically improved the luminescence properties and excitonic features. These improvements in annealed samples are mostly like by the reduction of defects and better crystallinity. Additionally, for the annealed samples, the absorption peaks for A, B excitons formed due to the valence band splitting were observed in absorption spectra at RT, as well as a small FWHM free emission in PL spectra. These results indicate that high quality ZnO thin films are prepared on SiO_2 substrates by RF magnetron sputtering with post-annealing.

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