Crystal structure and PL spectrum of ZnO films prepared by DC magnetic control sputtering

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ZnO is an n-type semiconductor having a hexagonal wurtzite structure. By X-ray diffraction (XRD) and scanning electron microscope (SEM), the influences of substrate temperature, the ratio of Ar to O_2 and thermal temperature on ZnO crystal quality were studied. The results show that ZnO films deaposited at substrate temperature of 240 °C and Ar:O_2=1:3 have the best crystallization. UV photoluminescence is observed when ZnO films are excited by He-Cd laser at room temperature. Stress at boundary causes an intrinsic UV emission peak shift to the lower energy. Oxygen vacancy or Zinc interstitial causes deep-level emission. With higher substrate temperature, the crystallization is improved and the stress and deep-level green emission are reduced.

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ZnO is a wide-band-gap Ⅱ—Ⅳ semiconductor with band gap energy of 3.37 eV. ZnO has received widespread attention in ultraviolet (UV) and blue emission as GaN due to its excellent quality such as high exciton bind energy (60 meV), low stimulated emission threshold, abundant material source, and little toxicity[1−3]. ZnO films is an n-type semiconductor, due to its higher optical-electrical couple coefficient, lower temperature coefficient, smaller dielectric constant, larger piezoelectric coefficient of C-axis-oriented ZnO, which can be used as acousto-electrical devices. On the other hand, ZnO is a promising material in making gas-sensors and so on. ZnO films have been grown by a variety of methods including radio-frequency (RF) sputtering chemical vapor deposition. In this paper, high quality zinc nitride films are grown successfully on Si substrate by rf-magnetron controlled sputtering. After annealing in O_2 ambience, we obtain high C-axis-oriented ZnO films. By studying the crystal structure and PL spectra, we have analyzed the emission mechanism[4,5].

ZnO films were made by rf-magnetron controlled sputtering method (JC500-310). The diameter of Zn target (99.999%) is 76.2 mm. We use Ar as the sputtering gas and O_2 as the reactant gas. The ratio of V (Ar) to V (O_2) is 1:3, which is controlled by different gas flow meters. The sputter power is 300 W and the film is 200-nm-thick. The crystal structure is studied by X-ray diffraction (XRD) spectrum (BD90X).

Figure 1(a) is XRD image of ZnO film grown at substrate temperature of 160 °C. One can see that ZnO film shows only on reflection: (002) at the 2θ angle of 34.4°. The full-width at half-maximum (FWHM) is 0.84°. which indicates that the ZnO film has a C-axis-oriented growth. When substrate temperature is 240 °C, XRD image shows only a (002) reflection, FWHM is only 0.34°, which shows ZnO film has a preferred C-axis-oriented growth. We find when substrate temperature is between 220 and 280 °C, ZnO films all have excellent film crystallinity. XRD images show only a (002) reflection, FWHM is smaller than 0.50°, which indicates that the substrate temperature increases, (002) reflection's FWHM decreases. The FWHM is smaller, the C-axis-oriented is more preferred. Gain size is larger, the film's crystallinity is more excellent. Temperature is too low or too high, ZnO has a larger FWHM and has some else reflections. Substrate temperature has a larger influence on ZnO films crystalline, this is because O atoms and Zn atoms absorbed on Si. Substrate have a low atom energy at a sufficiently low substrate temperature[6]. This causes atoms locates at lattic position before they reach the lowest energy position. So film has a bad crystallinity. On the other hand, the absorbed atoms have a large kinetic energy, O atoms desorb on the film surface. This always makes film have a bad crystallinity. We can draw a conclusion that substrate temperature locates only between 220 and 280 °C, which can make the absorbed atoms with proper energy reach the lowest energy lattic position. At the same time, the atoms have lower desportion rate and get the film processing excellent film crystallinity. Because ZnO (002)

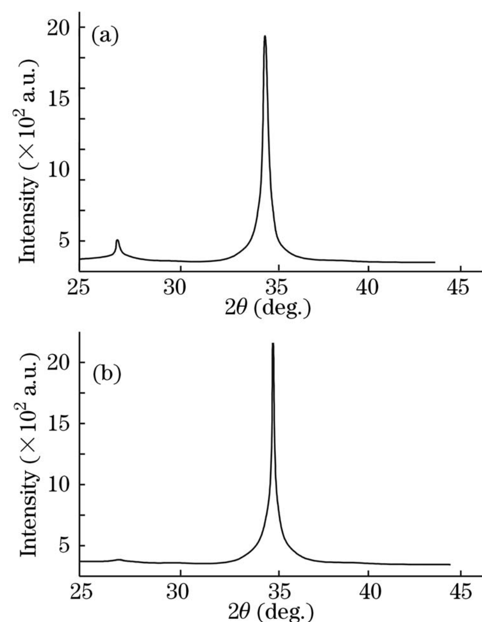

Fig. 1. XRD of ZnO films by magnetron sputtering with substrate temperatures of 160 (a) and 240 °C (b).

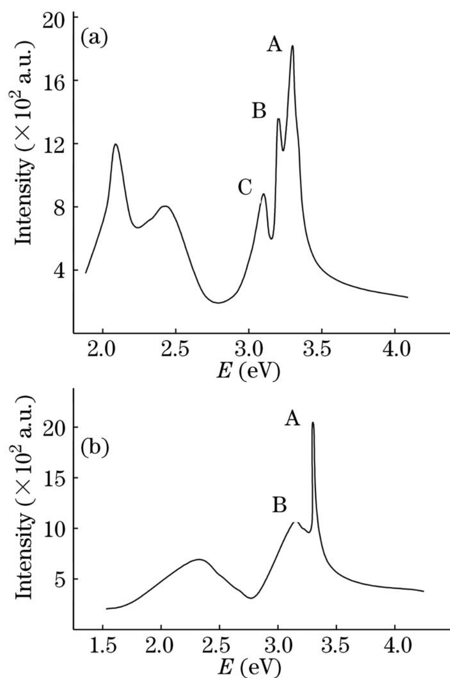

Fig. 2. PL spectra of ZnO film at room temperature with substrate temperatures of 160 (a) and 240 °C (b).

crystal's surface energy is the lowest when growth (002) crystal face becomes large and other crystal face is depressed, the film has a good C-axis-oriented growth. ZnO films are self-seambly charing deposition. The across-section of the column crystal is hexagon and the column crystal is vertical to the substrate. The films can be used as ultraviolet laser emission deuces[7].

Figure 2 shows the PL spectra excited by He-C laser (λ=325 nm, p=25 mW) at room temperature. The peak near 3.30 eV (named A) do not vary with temperature, which attributes to the band-gap of ZnO. The energies of peaks B and C is 3.05 and 3.20 eV, respetively. It shows that the mismatch of strain and lattice will narrow the band gap. We obtain ZnO films by directly current magnetron controlled sputtering method. The deposition rate is 30 nm per minute. When the growth temperature is lower, lateral growth is suppressed and the band gap is narrowed. As the substrate temperature increases from 160 to 280 °C, the peak disappears, and the intensity of peak B descends dramatically, and the intensity of peak A keeps stable. So the peak A corresponds to the band gap of ZnO films at room temperature. The XRD spectra show that the FWHM of the ZnO films is descended from 0.84° to 0.34°, which demonstrates that the rariety of peaks B and C are associated with interface stain. When the substrate temperature is lower, ZnO films is poorly preferred oriented and the C-axis of the column crystal is not paralle completely. During the film growth, intercrystal has a strong strain. When the growth temperature increases, we obtain high C-axis-oriented InO films. There are two emission in PL spectra, i.e., emission and green broad emission (2.2—2.5 eV). This green emission is attributed to the non-stoiochimetric of In and O atoms. The ratio of Zn atom to O atom is higher transunit, which tends to form O vacancy and In intersity atom. It brings donor level in the band gap. From PL spectra, there are two peaks located at 2.18 and 2.48 eV. With the increase of the substrate temperature, the peak shifts from 2.18 to 2.29 eV, while the peak at 2.48 eV is stable. The intensities of the two peaks drop down with increasing the substrate. So the peak at 2.48 eV is probably induced by film defect. Increasing the substrate temperature can lower the density of the defect, but it does not alter the deep leved position. The peak at 2.13 eV is due to the strain and its position which is associated to the release of the stain.

The C-axis-oriented ZnO films on the Si (100) substrate are attained by magnetic inputting. Through XRD, We found that the ZnO film appeares to be column, the FWHM is only 0.34°, the size of the crystallite is about 100 nm, we abseined the UV emission of ZnO film excited by photons. If the absentation is bad, the forbidden gaps of ZnO films caused by the interfaced stress move to long wavelength direction[8]. If the substrate temperature is higher, the interface stress will reduce, and the strain can be related. There is another advantage that higher substrate temperature can suppress the produce of impurities and defects. Thus the deep level emission of impurities and defects can be reduced.

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