Influence of TiO₂ Buffer on Structure and Optical Properties of ZnO Film on Si(100) Substrate

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ZnO films were prepared on p-Si (100) substrates by direct current (DC) sputtering with and without TiO₂ buffer. The crystal structures, surface morphologies and optical properties were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and photoluminescence (PL). XRD results indicated that the growth mode of ZnO film was changed from strong (002) preferential orientation to several crystal orientations by introducing TiO₂ buffer, and the residual strain was reduced. SEM manifested that ZnO film with TiO₂ buffer had the uniform grain size and flat surface. In addition, stronger ultraviolet emission was observed from ZnO film with TiO₂ than that without at room temperature. The low temperature photoluminescence was investigated to understand the different PL mechanism of ZnO films.

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1. Introduction

ZnO is a semiconductor with wide band-gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature. Generally, photoluminescence (PL) spectrum of single crystal ZnO at room temperature consists mainly of two bands. One in the UV region corresponding to the near-band-edge (NBE) emission at about 380 nm is mainly attributed to exciton states, and the other in the visible region is due to structural defects and impurities. In recent years, it has attracted much attention for possible applications in optoelectronic devices in ultraviolet region,¹⁻³⁾ and many groups dedicated to get high ultraviolet (UV) emission from ZnO film at room temperature. Some groups aimed at the preparation of high quality ZnO single crystal films.^{4,5)} As we know, it is difficult to find a cheap and suitable substrate to grow ZnO, high quality bulk ZnO substrate was very expensive and limited, which preclude their use in mass production environments. And for other substrates, there is a big lattice mismatch and the difference of thermal expand coefficient between the substrate and ZnO. Therefore, some researchers paid attention to the nanostructures of ZnO film or nanocomposition correlative to ZnO.⁶⁻⁸⁾ However, it was difficult to control the composition of nanostructures to get better result. In addition, some others enhance the ultraviolet emission by depositing ZnO films with different buffers, such as MgF₂, CaF₂, ZnO, GaN.⁹⁻¹²⁾ TiO₂ as a wide band-gap semiconductor has been widely investigated due to its high refractive index,¹³⁾ good photocatalytic behavior,¹⁴⁾ and high transparency in visible range.¹⁵⁾ Moreover, Cho and Lee¹⁶⁾ have obtained high quality rutile TiO₂ thin film using ZnO buffer layer on Si(100) substrate, it demonstrated that TiO₂ and ZnO can be taken as buffer each other. In the present study, strong ultraviolet emission at room temperature of ZnO film with TiO₂ buffer grown by DC reactive sputtering was firstly observed. And the samples were analyzed in detail by examining the XRD, SEM and PL.

2. Experimental Procedure

ZnO films with TiO₂ buffer and without were deposited by DC reactive sputtering method on p-type Si (100) substrates using pure Zn (99.99%) and Ti (99.99%) target. The distance from substrate to target was kept at 5 cm. The TiO₂ buffer layer and ZnO film have the same deposition conditions including the Ar/O₂ (3/1), sputtering time (40 min), bombardment voltage (2.8 KV) and substrate temperature (300°C). The thicknesses of TiO₂ buffer and ZnO film are about 20 nm and 150 nm, respectively. At last, the obtained films were annealed at 900°C for 1 h in O₂ ambient. We named the ZnO thin films on bare substrate and TiO₂ buffer layer as a and b.

The X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Japan D/Max-rA X-ray diffractometer). The surface morphologies were observed from field emission scanning electron microscopy (FESEM) images taken on a JEOL FESM-6700 field emission scanning electron microanalyzer. PL spectra were measured at room and low temperature with the excitation source of the 325 nm line of a He-Cd laser.

3. Results and Discussion

Figure 1 shows the XRD patterns of ZnO films with and without TiO₂ buffer on p-Si substrates. It can be seen that the two ZnO films exhibit strong *c* axis preferred orientation, the values of full width at half maximum (FWHM) of (002) diffraction peaks are both 0.36°. Whereas, the diffraction peaks of (100), (101) and (110) have also been observed for sample b, and the intensity of (002) diffraction peak weakens apparently compared to sample a. The results may be explained as follows, when the ZnO film was grown with TiO₂ buffer, the effect of Si substrate on growth orientation of ZnO film became very weak, the nucleation and crystal growth may have occurred throughout the films without being initiated exclusively on the substrate surface.¹⁷⁾ Thus, ZnO didn't just grow along *c* axis any more, and along several directions freely.

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Fig. 1 XRD patterns of ZnO thin films (a) on bare Si substrate (b) with TiO₂ buffer.

It is worthy to note that the position of (002) diffraction peak shifts from 34.744° to 34.431°. Based on the X-ray diffraction theory: $2d \sin \theta = \lambda$, where d is the space between (002) planes; λ the X-ray wavelength (0.154 nm); θ the Bragg diffraction angle, the crystal lattice constant $c = 2d$ can be calculated. The calculated c is 0.5157 nm for sample a and 0.5203 nm for b. As we know, the crystal lattice constant c for power ZnO crystal is 0.5209 nm. Thus, the ZnO film with TiO₂ buffer has the more similar c length with the powder ZnO. Therefore, the strain in ZnO film can be calculated by equation:^{18,19)}

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \frac{c - c_0}{c_0} \quad (1)$$

The values of the elastic constant for single crystalline ZnO are used, $c_{11} = 208.8$ GPa, $c_{33} = 213.8$ GPa, $c_{12} = 119.7$ GPa and $c_{13} = 104.2$ GPa. Substituting these values in the above equation gives $\sigma = -233(c - c_0/c_0)$ GPa. The strain calculated was $+2.32 \times 10^9$ Pa for ZnO film without buffer layer, and $+2.68 \times 10^8$ Pa for that with TiO₂ buffer. The positive sign indicated that the lattice constant c was compressed compared to unstressed powder, and ZnO film was in a state of compression. In general, the origin of compressive stress generally comes from two kinds of defects, one is lattice dislocation resulting from the difference of the thermal expansion coefficient and lattice mismatch between Si and ZnO, and the others are grain boundaries and intrinsic point defects coming from the course of crystal growth. If the ZnO films were deposited on bare Si substrates directly, there would be a large compressive stress resulting from the lattice mismatch and the difference of thermal expansion coefficient. When we introduced TiO₂ buffer which was deemed to be amorphous with small thickness, the crystal grains of ZnO grew more freely avoiding the influence of Si substrate, as indicated by XRD results. And the compressive strain was released due to the flexible TiO₂ buffer layer. Therefore, the strain in the ZnO film decreased by using TiO₂ buffer, and the quality of epitaxial ZnO layer far away from the interface was improved.

Figure 2 shows the surface morphology images of ZnO films on bare Si substrate and with TiO₂ buffer. For that with buffer (Fig. 2(b)), it is covered with uniform grains with diameter of 200–300 nm. As to Fig. 2(a), there are not only uniform crystals with diameter of 200–300 nm, but also many large crystal rods with length of 1.5 μm interspersing

Fig. 2 Scanning electron microscope images of ZnO thin films (a) on bare Si substrate (b) with TiO₂ buffer.

Fig. 3 PL spectra of ZnO thin films (a) on bare Si substrate (b) with TiO₂ buffer at room temperature.

above the layer of uniform crystal. Thus, the sample a has the much rougher surface and higher density grain boundaries associated with the worse crystallites.

PL spectra of ZnO films on Si (100) substrates with and without TiO₂ buffer layer measured at room temperature were shown in Fig. 3. For the two samples, PL spectra show only one strong UV emission at 384 nm; and no other obvious visible bands in the PL spectra resulting from structure defects and impurities. The absence of the visible light emission in the samples implied that both the ZnO films were of low defects density and excellent optical quality. Besides, the intensity of UV emission for sample b is stronger than sample a, the increase in the intensity of UV emission implied that the radiative recombination efficiency of ZnO was improved due to TiO₂ buffer on the Si substrate. And the FWHMs of UV emission peaks changed from 154 meV to 133 meV for sample a and b. It may be concluded that the sample has much better crystal quality by introducing TiO₂.

Fig. 4 PL spectra of ZnO thin films (a) on bare Si substrate (b) with TiO₂ buffer at 10 K.

Subsequently, in order to investigate the PL mechanism of UV region in ZnO films, we measured PL spectra for these two samples at 10 K, which were shown in Fig. 4. It can be seen that the PL spectra of them both consist of three peaks; which have been observed previously by many authors.²⁰ In sample b, the strong and sharp peak at 3.351 eV can be assigned to bound exciton emissions at neutral donors (D⁰X),²¹ usually, the energy region from 3.310 to 3.351 eV is expected to be related to the two electron satellite (TES) recombination lines of D⁰X.²² For sample a, the emission intensity is much weaker than b and the three main peaks were much wider. The emission line at 3.378 eV is related to free exciton emission (FX). And for 3.327 eV line, the energy spacing between 3.378 and 3.327 eV is 51 meV, which is consistent to the TO phonon replica (51 meV) of FX. However, the intensity of line at 3.327 is much larger than that at 3.378. So the 3.327 eV line should not come from the phonon replica of FX. Xu *et al.*²³ have reported the similar phenomenon, and demonstrated that the line is the counterpart of FX leaving the donor ionized, defining as FX-D effect. As for line 3.257 and 3.261 eV in sample a and b, they could be suggested as radiative recombination related to donors and acceptors. As described above, sample a and b have the different photoluminescence mechanism at low temperature, which is corresponding to their different crystal quality. Thus, the sample b had the better radiative recombination efficiency.

4. Conclusions

In summary, ZnO film with TiO₂ buffer has been prepared by DC reactive sputtering. The influences of TiO₂ buffer on structure and PL properties of ZnO films were studied. The XRD results demonstrated that ZnO films were hexagonal wurtzite structure with highly *c*-axis orientation, and the residual stresses in ZnO films were released by introducing TiO₂ buffer. In particular, the sample b had much stronger ultraviolet emission than sample a, the different optical property may result from the different photoluminescence

mechanism, which is corresponding to the crystal quality of samples. In sample a, the counterpart of FX leaving the donor ionized, defining as FX-D effect, dominated the low temperature PL spectra, and for sample b, the neutral-donor bound exciton emission dominated.

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