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Review

Pure UV photoluminescence from ZnO thin film by thermal retardation and using an amorphous SiO_2 buffer layer

Linxing Shi [a,*], Xiangyin Li [b]

[a] School of Sciences, Huaihai Institute of Technology, Lianyungang 222005, PR China
[b] Department of Physics, Nanjing University of Science and Technology, Nanjing 210094, PR China

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ABSTRACT

ZnO/SiO_2 thin films were fabricated on Si substrates by E-beam evaporation with thermal retardation. The as-prepared films were annealed for 2 h every 100 °C in the temperature range 400–800 °C under ambient air. The structural and optical properties were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL). The XRD analysis indicated that all ZnO thin films had a highly preferred orientation with the *c*-axis perpendicular to the substrate. From AFM images (AFM scan size is 1 μm × 1 μm), the RMS roughnesses of the films were 3.82, 5.18, 3.65, 3.40 and 13.2 nm, respectively. PL measurements indicated that UV luminescence at only 374 nm was observed for all samples. The optical quality of the ZnO film was increased by thermal retardation and by using an amorphous SiO_2 buffer layer.

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1. Introduction

Recently, a great deal of attention has been paid to ZnO as its properties offer great potential, i.e. a large band-gap energy of 3.37 eV for the wurtzite structure at room temperature and large exciton binding energy of ~60 meV. ZnO has also been employed in a vast range of devices including short wavelength light emitting diodes [1], and photodetectors [2]. Substrate selection is a crucial issue in ZnO growth. Silicon (Si) is the most suitable substrate not only because of its low cost but also for its additional advantages in integrated photoelectronic devices. However, direct growth of ZnO films on Si is extremely difficult and often results in amorphous or polycrystalline films due to the mismatch of large lattice and thermal expansion coefficients between ZnO and Si. Films deposited on a buffer layer are better than those grown directly on the Si substrate. Many different buffer layers such as MgO [3], SiC [4] and MgF_2 [5] have been employed. ZnO is a promising material for light emitters in the UV region. The optical quality of ZnO, which is expressed as the ratio of the peak intensities of near band-edge emission (I_{NBE}) to that of deep-level emission (I_{DL}), that is I_{NBE}/I_{DL}, is a key aspect for studying the applications of ZnO film in the UV region. Kumano et al. [6] obtained a ratio as high as 60 even at room temperature. Zhao et al. [7] reported an intensity ratio of 122 for thin films prepared at 650 °C by pulsed laser deposition (PLD).

In this paper, ZnO films were fabricated on Si substrates by E-beam evaporation using SiO_2 as the buffer layer. Thermal retardation for 30 min at a temperature of 300 °C, higher than the deposited temperature of 250 °C, was used to increase the optical quality of the ZnO film. UV emission was observed at only 374 nm. Furthermore, the influence of the annealing temperature on the as-prepared ZnO/SiO_2 film has been investigated in detail.

2. Experimental

ZnO/SiO_2 films were grown on Si substrates by E-beam evaporation (PMC90S, Protech Korea Ltd). SiO_2 and ZnO were

* Corresponding author. Tel.: +86 518 85895508.
E-mail address: slxopt@hotmail.com (L. Shi).

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deposited at 250 °C. The chamber was evacuated to a base pressure of 2.0×10^{-5} Torr, then Ar (purity: 99.9999%) at 18 SCCM (cubic centimeter per minute at STP) was used to etch the substrates for 5 min. Then, a flow of O_2 (purity: 99.9999%) at ~17 SCCM for SiO_2 and ~20 SCCM for ZnO was turned on. The electron gun voltage was 7.10 kV for depositing both ZnO and SiO_2. The current was 30 mA for ZnO and 89 mA for SiO_2. The deposited sources of ZnO and SiO_2 were 99.999% pure. SiO_2 films were deposited at a rate of 5.2 Å/s, while 3.2 Å/s was used for ZnO films. Each layer was ~200 nm thick. Finally, the chamber temperature was raised from 250 to 300 °C for 30 min after the films were deposited. Subsequently, the as-deposited films were annealed in a tube furnace for 2 h every 100 °C in the temperature range of 400–800 °C under ambient air.

The structures of the films were characterized by a Bruker D8-advance X-ray diffractometer with Cu K_α (λ=1.5406 Å) radiation. The 2θ range used in the measurements was 10–70° in steps of 0.02° s^{-1}. AFM images were collected using a CSPM4000 scanning probe microscope system (Benyuan Nano-Instruments Co. Ltd., Beijing, China). PL spectra were acquired with a FluoroMax-2 fluorescence spectrometer (JOBIN YVON-SPEX) at 350–600 nm, with a 325 nm (Xe lamp) excitation light. The photoluminescence excitation (PLE) spectra were measured in the interval 300–400 nm with a detection wavelength of 374 nm. All measurements were performed in air at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnO thin films. Whether the films were annealed or not, only the (0 0 2) peaks were observed, which shows that the ZnO thin films have a highly preferred orientation with the *c*-axis perpendicular to the substrate. No SiO_2 diffraction peaks were observed in the films. This means that SiO_2 is amorphous in those samples. Unlike ZnO films on crystalline substrates, there is no epitaxial relationship between the ZnO thin films on the SiO_2 buffer layer. From the full-width at half-maximum (FWHM) and the peak position of the (0 0 2) peak, the grain sizes in the films can be estimated with the Scherrer formula. Calculation of the film stress is based on the biaxial strain model [8]. Grain sizes and biaxial stresses, calculated from (0 0 2) peak positions, are shown in Table 1. The interplanar spacing parameters are smaller than d_0 (2.6035 Å, is the strain-free interplanar spacing) and compressive stresses are

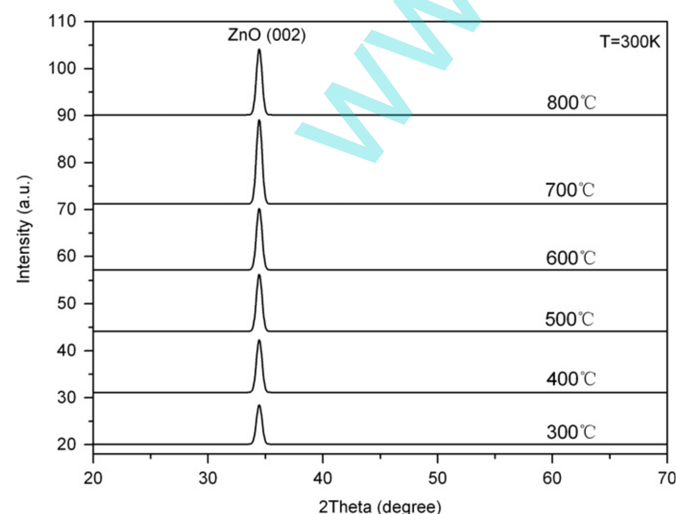

Fig. 1. XRD patterns of ZnO thin films on Si substrate using SiO_2 as buffer layers and at different annealing temperatures.

Table 1
Data evaluated from XRD and AFM for samples with different annealing temperatures.

Sample	*2θ (deg.)*	*Interplanar spacing d (Å)*	*FWHM (deg.)*	*Graininess (Å) XRD*	*Graininess (Å) AFM*	σ_{film}(GPa)
as-prepared	34.481	2.5990	0.383	218	215.6	0.4027
400 °C	34.480	2.5990	0.314	266	243.6	0.4027
500 °C	34.581	2.5917	0.355	235	205.8	2.7494
600 °C	34.641	2.5873	0.330	253	215.0	3.7746
700 °C	34.561	2.5931	0.311	269	263.3	2.4232
800 °C	34.561	2.5931	0.300	278	432.0	2.4232

induced because of differential thermal expansion between ZnO and the SiO_2 buffer layer. The grain sizes and compressive stresses increase with increase in annealing temperature.

Fig. 2 shows AFM images of the samples. In Fig. 2(a), the very smooth surface of the as-prepared sample can be seen. The Root Mean Square (RMS) roughness is 3.82 nm. This can be explained by migration of the surface atoms and the release of stress (0.4027 GPa) due to thermal retardation. The surface morphology became rougher and the RMS roughness of the film increased from 3.82 to 5.18 nm when the annealing temperature was 400 °C. This is ascribed to inadequate growth of the grains and the existence of agglomerated particles. When the annealing temperature was increased from 500 up to 700 °C, the surfaces of the samples became smooth and the RMS roughnesses were 3.65, 3.58 and 3.40 nm, respectively. The boundaries of the grains became clear and the grain sizes increased with increase in annealing temperature. But the stresses in the films are obviously increased because of the introduction of grain boundaries. The surface of the film has been scorched when the annealing temperature was 800 °C. The RMS roughness was 13.2 nm and this is significantly larger than the values for the other samples.

Generally, PL spectra from ZnO consist of the UV emission band and the visible emission broadband. UV emission is attributed to exciton recombination. The visible luminescence is mainly due to structural defects, which are related to deep-level emissions, such as zinc vacancies, oxygen vacancies, interstitial zinc and interstitial oxygen. Fig. 3 illustrates the PL spectra at 350–600 nm and the PLE spectra at 300–400 nm for the ZnO/SiO_2 thin films. In Fig. 3(a), UV luminescence at 374 nm is observed for all samples. The peak positions of UV emissions from ZnO films do not change with the increase in annealing temperature. This is because of the presence of abundant oxygen when ZnO is being deposited. More importantly, thermal retardation was carried out for 30 min at 300 °C after ZnO had been deposited. Meanwhile, the ZnO thin films have a highly preferred orientation with the *c*-axis perpendicular to the substrate from the XRD results, and the surfaces of the films are quite smooth from the AFM images. The annealing treatment merely introduced some redistribution and a slight growth of the ZnO grains in the films, but it did not change the structure of the films. So, the intensity of the UV emission at 374 nm increased with increase in annealing temperature up to 700 °C, while the intensity of UV emission decreased when the annealing temperature was 800 °C. In Fig. 3(b), in the PLE spectra of ZnO thin film monitored at 374 nm, the peak positions are all at 328 nm. This is consistent with the PL results. Apart from thermal retardation, there is a relationship between UV emission and the crystallinity of the buffer layer. In our experiments, the SiO_2 buffer layer is amorphous. There must be some relationship between ZnO films and the crystallized buffer layer. For example, in our previous report [9], co-emission of UV, violet and green luminescence was observed from ZnO film deposited on a crystalline TiO_2 buffer layer. Similar results were reported for visible luminescence from ZnO film [10,11].

Fig. 2. AFM images of the samples: (a) as-prepared, (b) 400, (c) 500, (d) 600, (e) 700 and (f) 800 °C.

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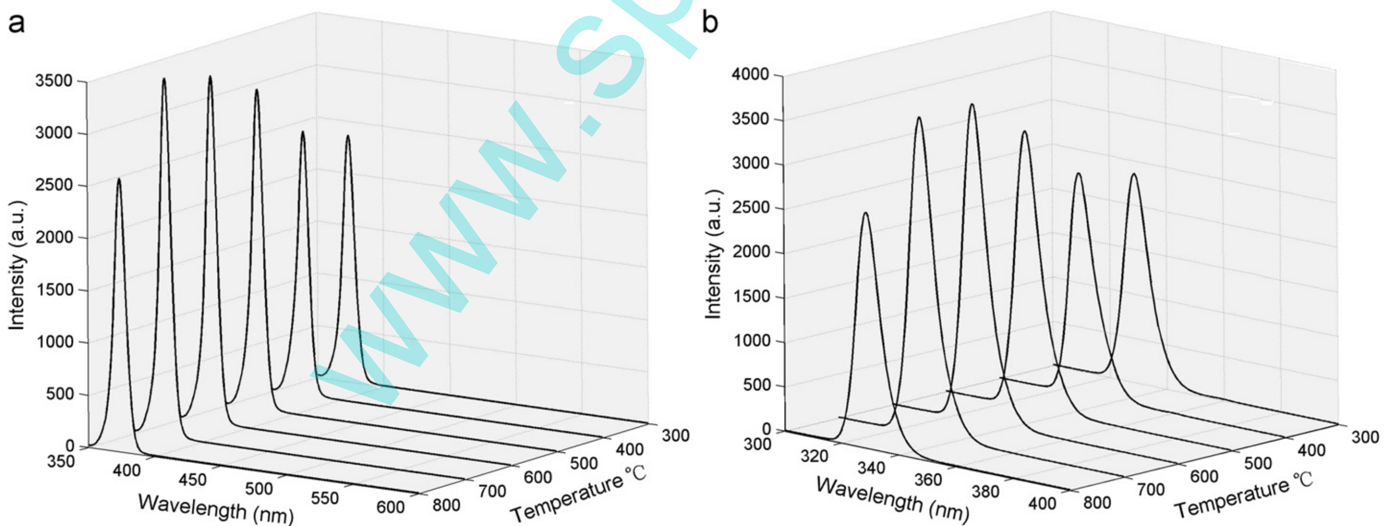

Fig.3. Room temperature PL and PLE spectra of ZnO thin film grown on Si substrates using SiO_2 as buffer layer: (a) PL and (b) PLE spectra.

4. Conclusions

ZnO/SiO_2 thin films on Si substrates were fabricated by E-beam evaporation. Thermal retardation for 30 min at a temperature of 300 °C, higher than the deposited temperature of 250 °C, was used to increase the optical quality of the ZnO film. XRD demonstrated that the as-prepared and annealed ZnO thin films have a highly preferred orientation with the *c*-axis perpendicular to the substrate. The SiO_2 buffer layer is amorphous. AFM images illustrated that the surfaces of the thin films were very smooth. The RMS roughnesses of the films were 3.82, 5.18, 3.65, 3.58, 3.40 and 13.2 nm, respectively. PL spectroscopy showed that UV luminescence at only 374 nm is observed for all samples. The intensity of the UV emission at 374 nm increased with increase in annealing temperature up to 700 °C. The optical quality of the ZnO film has been improved by thermal retardation and by using an amorphous SiO_2 buffer layer.

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