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Influence of growth temperature on the optical and structural properties of ultrathin ZnO films

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ABSTRACT

This study investigates the effect of growth temperature on the optical and structural properties of ultrathin ZnO films on the polished Si substrate. Thickness of the ultrathin ZnO films deposited by atomic layer deposition (ALD) method was about 10 nm. Photoluminescence (PL), X-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques were used to measure the properties of ultrathin ZnO films. Experimental results showed that the ultrathin ZnO film deposited at 200 °C had excellent ultraviolet emission intensity, and the average roughness of the film surface was about 0.26 nm.

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1. Introduction

ZnO is a wide-band gap semiconductor (3.37 eV at room temperature) with a large exciton binding energy of 60 meV, which is twice as high as GaN (21 meV) or ZnSe (20 meV). Moreover, ZnO is thermally and chemically stable at room temperature and is a good piezoelectric and semiconductor material. In addition, ZnO films with doping have transparency [1]. ZnO can be applied in optoelectronic and piezoelectric devices, such as transparent electrodes [1], varistors [2], piezoelectric transducers [3], gas sensors [4], ultraviolet photodetectors [5] and surface acoustic wave devices [6]. Recently, ZnO thin films with high crystal quality are required for manufaturing high performance optoelectronic nanodevices. Several deposition techniques have been used to deposit ZnO thin films, including chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and pulsed laser deposition (PLD) [7–11]. These approaches, however, require either high growth temperature (over 400 °C) or post-annealing at high temperature (over 500 °C).

The deposition of ultrathin ZnO film (<30 nm) is faster and less expensive, though there is a lack of research on the effect of growth temperature for the characteristics of ultrathin ZnO films. Thus in this study, the influence of growth temperature on the optical and structural properties of ultrathin ZnO films is investigated in detail. The ultrathin ZnO films were deposited on a polished Si substrate at the growth temperature of 25, 50, 100 and 200 °C using ALD and the samples did not need post-annealing.

2. Experimental

The ultrathin ZnO films were deposited by ALD on a polished Si (1 0 0) substrate at the temperature of 25 °C. ALD is a growth film technique that employs a self-limiting vapor-phase chemisorption depending on consecutive surface reactions. It applies critical purge steps to prevent interactions between the reactive precursors. The pulse durations of water and diethylzinc (DEZn) were 90 ms and 45 ms, respectively. The purge and pumping periods were 15 s and N_2 was used as the purge gas with the pressure being set at 3×10^{-2} Torr. In this practice, the films are grown in a monolayer-by-monolayer fashion. The ALD process was used for depositing ultrathin ZnO films on the surface of polished Si substrate, and the ZnO film thickness was estimated to be about 10 nm with 35 ALD cycles. As described later in the experimental results, the intensity of near band-edge emissions from the ultrathin ZnO films deposited at 200 °C can be significantly improved over the ultrathin ZnO films deposited at 25, 50, and 100 °C.

The structural characteristics of the ultrathin ZnO films were determined by XRD technique using Cu Kα radiation (λ = 1.54 Å) (PANalytical X'Pert Pro, Philips X'Pert Inc.), which was operated at 45 kV and 40 mA for grazing angle scan. In additionally, TEM (JEOL JEM-2010F Japan) with an operating voltage of 200 kV and energy dispersive X-ray spectroscopy (EDS) were used to examine the microstructure and composition of samples. Tapping-mode AFM (Veeco Dimension 5000, USA) was utilized to measure the surface morphologies of the ultrathin ZnO films at a constant frequency of 1.0 Hz. In addition, photoluminescence (PL) was measured at room temperature using a He–Cd laser (325 nm) for excitation and a CCD with a monochromator for detection.

3. Results and discussion

To characterize the effect of growth temperature for ultrathin ZnO films, the grazing incidence XRD technique was employed to

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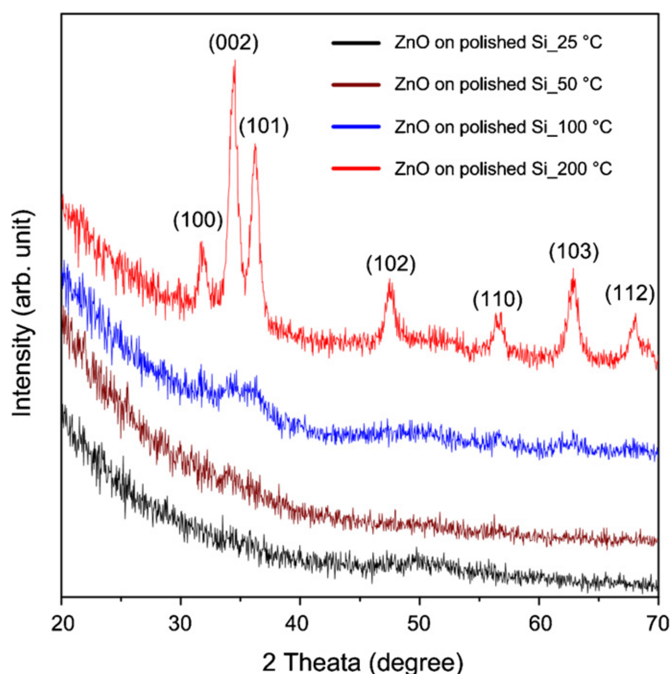

Fig. 1. XRD spectra of ultrathin ZnO films deposited at 25, 50, 100 and 200 °C.

examine ultrathin ZnO films. Fig. 1 shows the XRD curves obtained for the ZnO films with thickness of 10 nm at the growth temperatures of 25, 50, 100, and 200 °C. For the ZnO film deposited on polished Si substrate at 200 °C, the strongest diffraction peak appeared in the 2θ of 34.4°, corresponding to the (0 0 2) diffraction. In addition to (0 0 2) diffraction, there were many other diffraction peaks in the XRD curve, indicating the ultrathin ZnO film deposited on polished Si at 200 °C was polycrystalline.

Grain size is a very important structural characteristic for all thin films since carrier motilities are influenced by polycrystalline grain sizes and boundary barrier heights. The Fermi level at grain boundaries is changed when carriers trapped at grain boundaries locally change [12], and barriers at grain boundaries are created by a Fermi level change that impedes conduction. Thus, the average grain sizes of ultrathin ZnO films were calculated by Eq. (1) [13]:

$$L = \frac{k\lambda}{B\cos\theta} \qquad (1)$$

where L represents the linear dimension of grain size, B is the full-width-half-max (FWHM) of the peak, λ is the wavelength of the incident X-rays (using λ = 0.154 nm X-ray), θ is the Bragg angle and k is a numerical constant value 0.9. Accordingly, Eq. (1) yields the average grain size of an ultrathin ZnO film. Investigations showed that the mean grain size of the ZnO films was 13.7 and 17.6 nm at the growth temperatures of 100 and 200 °C, respectively. That is to say, the ZnO quality can be improved by increasing growth temperature to 200 °C. For the ZnO films deposited at 25 and 50 °C, the peaks in the same range of diffraction angles were much weaker and were no longer distinguishable, indicating that the ultrathin ZnO films deposited on the Si substrate are probably largely amorphous.

Fig. 2(a) displays the HRTEM image for the 10 nm thick ZnO film deposited on the polished Si substrate at the temperature of 200 °C using ALD with diethylzinc (DEZn) and water as reactants. It can be seen that the ZnO layer was uniformly deposited on the polished Si and there were regions showing ZnO nano-crystals within the ZnO layer, marked by the dashed circle in Fig. 2(b). This result is in agreement with the XRD results shown in Fig. 1, where the ultrathin ZnO films deposited on a polished Si substrate at 200 °C had a stronger diffraction peak corresponding to ZnO crystalline

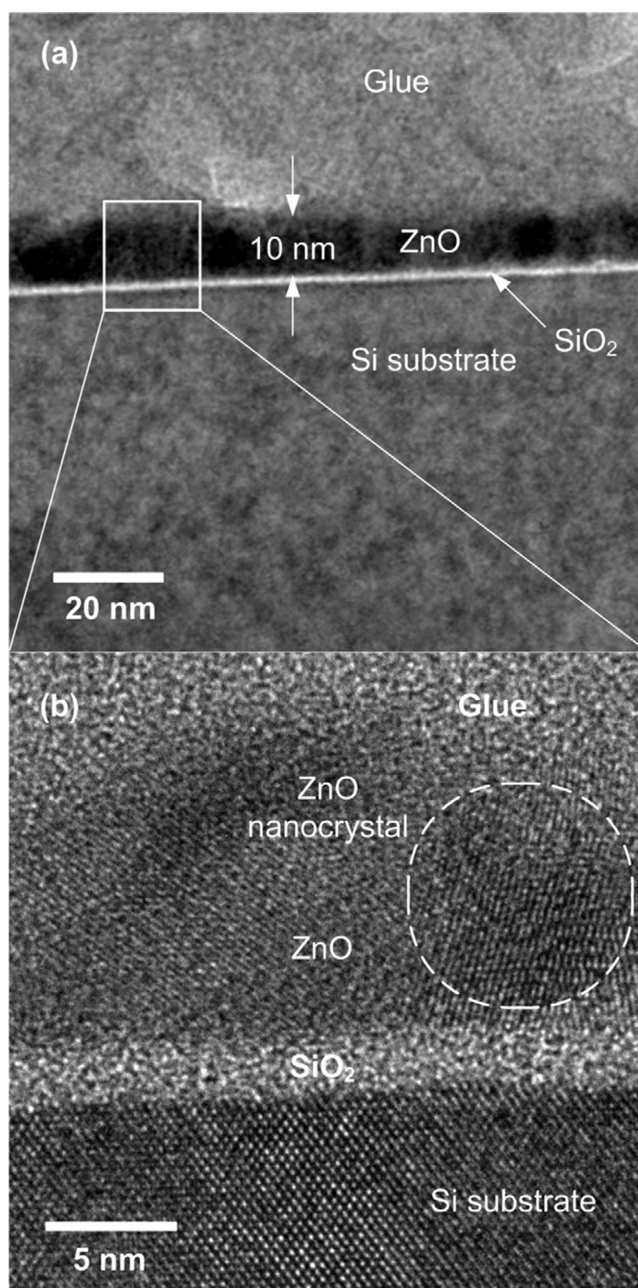

Fig. 2. The (a) TEM and (b) high-resolution TEM image of ultrathin ZnO films deposited at 200 °C.

phase. In other words, the ZnO crystalline quality increased as the substrate temperature increased. The improved quality of the ZnO film was attributed to sufficient thermal energy for reactants to achieve equilibrium atomic sites under such conditions.

The electronic transport features depend on the surface roughness of the thin films [14,15], and thin films with poor surface morphology strongly degrade the performance of electronic devices. Thus, a very smooth surface topography for ZnO films is essential. Fig. 3 presents the AFM images for the morphology of the ultrathin ZnO films with different growth temperatures. In this investigation, the area of 5 μm × 5 μm was observed and the mean roughness of the ZnO films was measured. As shown in Fig. 3(a), the ZnO film deposited at 25 °C had a surface covered by ridge-shaped islands, and the average roughness (R_a) of surface was as high as 0.91 nm. As illustrated in Fig. 3(b), only a few islands were found on the surface of the ZnO film deposited at 200 °C, and the aver-

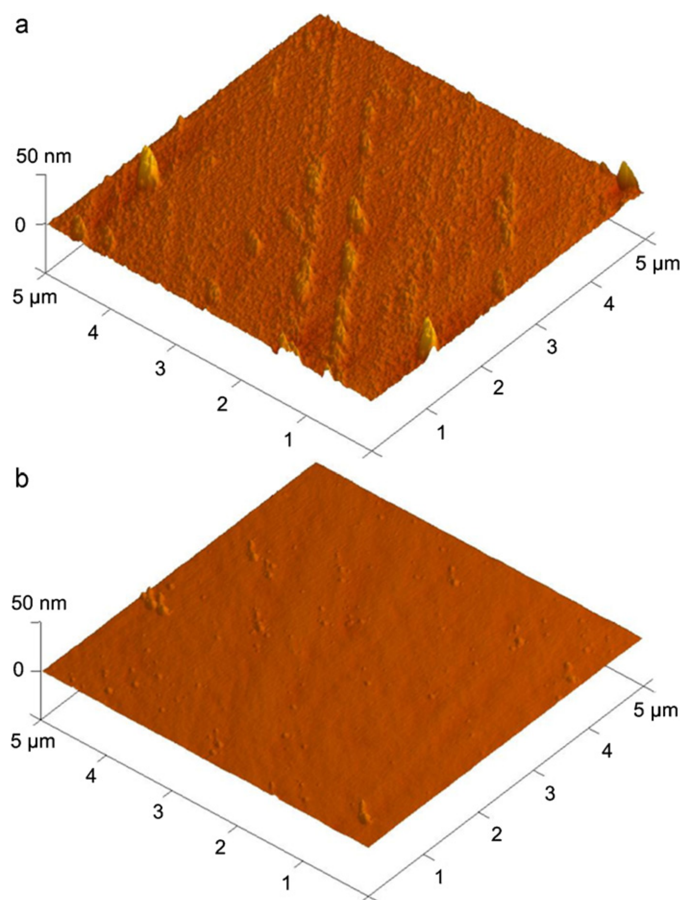

Fig. 3. AFM images of the ultrathin ZnO films deposited at the growth temperature of (a) 25 °C, and (b) 200 °C.

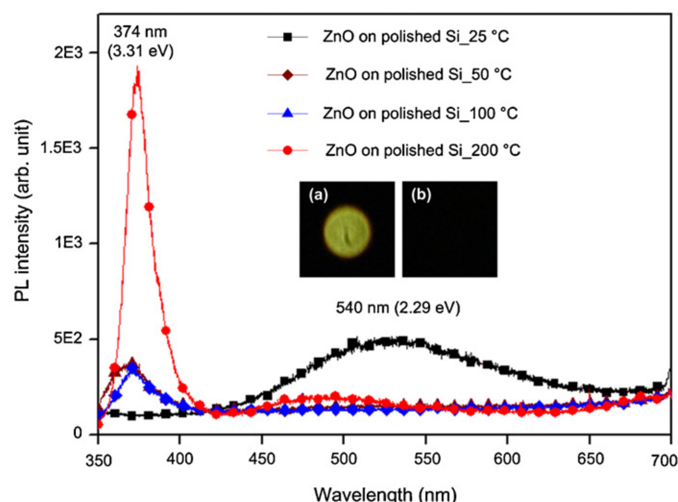

Fig. 4. The PL spectra of the ZnO films. The insets (a) and (b) show the luminescence taken from ZnO films deposited at 25 °C and 200 °C, respectively.

age roughness of surface was 0.26 nm. Comparing to the results shown in Fig. 3(a), the ZnO film deposited at 200 °C had excellent surface roughness. That is to say, growth temperature can effectively control the surface roughness of the ZnO films. The smooth surface of the ZnO film deposited at 200 °C was attributed to higher growth temperature reducing the density of defects such as vacancies or interstices. The ZnO film, presented by Purica et al. [16], was deposited on InP substrate by single source chemical vapor deposition (SSCVD) at growth temperature of 360 °C, and the average roughness of the film was 1.31 nm. Weng et al. [17] used the electrochemical deposition to grow ZnO on the indium tin oxide (ITO)-covered glass substrate at growth temperature of 70 °C, and then the film was annealed in air at 500 °C for 1 h, which its average roughness was 55.20 nm. A comparison of the above literatures, the average roughness of this work (0.26 nm) exceeds that of Purica et al. [16] and Weng et al. [17].

In order to understand the optical properties of the ultrathin ZnO films deposited on polished Si substrate at different temperatures, the PL spectra of the ultrathin ZnO films were examined, and the results are shown in Fig. 4. We first discuss the ultrathin ZnO film deposited at 25 °C, whose spectrum showed no peak in the UV regime (solid squares). Moreover, according to this PL curve, a broadened spectrum covering the entire visible region and peaking around 540 nm (2.29 eV, in the green emission regime) was observed. Indeed, as shown in the inset (a) of Fig. 4, the pictures taken by digital camera clearly exhibits the green emission. As mentioned above, the visible PL emissions observed in various ZnO structures have been the subject of extensive research [18–21] and it was generally considered that the green PL emission in ZnO is primarily due to oxygen-related defects residing near the surface [22,23]. This is to say, the visible emission is attributed to donor–acceptor-pair transitions involving oxygen vacancy.

Regardless of the precise origin of the green emission, the strong visible PL intensity indicated that the ultrathin ZnO film deposited at 25 °C was rich in atomic defects. Due to the low growth temperature of 25 °C, samples with high crystalline quality were difficult to obtain. As the ZnO films grew at a low growth temperature, the excitons were usually localized by potential fluctuations or trapped at intrinsic defects in the thin films. Such exciton localization or trapping helps to prevent exciton transition to the centers of nonradiative decay. On the other hand, the ZnO films deposited at 200 °C strongly decreased the formation of intrinsic defects such as vacancies, so the excitons became mobile and achieved centers of nonradiative decay. This is evidence that ALD with higher growth temperature can obtain high quality ultrathin ZnO films with inefficient nonradiative decay channels and with thermodynamically blocked self-compensation processes. According to the PL measurements, the intensity of UV emission increased with increasing growth temperature to 200 °C, and the visible emission was almost suppressed (shown in Fig. 4, solid circles), indicating the ZnO film has high quality. The PL result was in good agreement with the XRD and TEM measurements, as shown in Figs. 1 and 2. It is important to note that, under growth temperature of 200 °C, the intensity of UV emission from the ZnO film deposited on polished Si has more than one order of magnitude enhancement in the intensity of the room temperature PL peak around 374 nm compared to that from the ZnO film deposited on polished Si at the growth temperature of 25 °C. The inset (b) in Fig. 4 shows a dark picture (by digital camera) for ZnO film deposited at 200 °C because the UV emission cannot be detected by naked eyes.

4. Conclusion

In summary, we have demonstrated that, by properly manipulating the growth temperature, the ALD technique could obtain the ultrathin ZnO films of high quality. Based on TEM observation, the ultrathin ZnO film deposited at the growth temperature of 200 °C had polycrystalline structure. Moreover, the results of AFM measurement show the average roughness of the ZnO films deposited at 200 °C was about 0.26 nm. The UV emission intensity of ultrathin ZnO film was strongly enhanced by increasing the growth temperature to 200 °C, indicating that the quality of ZnO film was significantly improved.

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