Rapid Communication

In situ high temperature X-ray diffraction studies of ZnO thin film*

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An epitaxial ZnO thin film was entirely fabricated by pulsed laser deposition. Both the orientation and the size of the crystallites were studied. The X-ray diffraction (XRD) patterns of the film show strong *c*-axis oriented crystal structure with preferred (002) orientation. The Phi-scan XRD pattern confirms that the epitaxial ZnO exhibits a single-domain wurtzite structure with hexagonal symmetry. *In situ* high-temperature XRD studies of ZnO thin film show that the crystallite size increases with increasing temperature, and (002) peaks shift systematically toward lower 2θ values due to the change of lattice parameters. The lattice parameters show linear increase in their values with increasing temperature.

Keywords: high temperature XRD, ZnO thin films, lattice parameters, pulsed laser deposition

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1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor and has been extensively investigated due to its potential utility in various applications such as in solar cells,[1] transparent electrodes,[2] blue/UV light emitter device,[3,4] gas sensor,[5] and transducer.[6] The notable properties of ZnO are its wide direct band gap (3.37 eV at room temperature) and high exciton binding energy of 60 meV.[7] This large exciton binding energy provides excitonic emission more efficiently even at high temperature. The ZnO also has high thermal and chemical stability.[8,9] Due to the various attractive properties and potential applications of ZnO, there has been much attention paid to ZnO films in recent years.[10−12]

In this paper, *in situ* high temperature X-ray diffraction (XRD) studies were performed in the temperature range varying from room temperature to 900°C to study the effect of temperature on phase, crystallite size and lattice constants of ZnO thin film.

2. Experiment

In this work, the ZnO thin film was grown on Si (111) by pulsed laser deposition (PLD). The PLD target was prepared by zinc oxide (ZnO) powder evenly pressing and sintering, and the purity of ZnO powder was 99.999%. In the PLD growth chamber, there were four rotated targets and a substrate base, and the distance between the target and the substrate was about 80 mm. The background vacuum was up to 4×10^{-4} Pa in the growth chamber. The KrF laser with the wavelength of 248 nm was used at an incident angle of 45° to the target. The specific growth conditions were as follows: the laser pulse energy was 200 mJ per pulse, the pulse frequency was 5 Hz, the deposition time was 40 min, and the substrate temperature was 500°C.

The XRD measurements of *in situ* high temperatures were performed on the U7b beamline at the National Synchrotron Radiation Laboratory. A Si (111) double-crystal monochromator was used to select a wavelength of 1.29 Å within an energy resolution of $\Delta\lambda/\lambda = 5 \times 10^{-4}$. The beam size was collimated to 1 mm (horizontal) by 0.5 mm (vertical). The temperature in the sample holder was controlled within 1°–2° Celsius. The sample temperature was measured by a Pt-10%Rh-Pt thermocouple with its junction located at the sample holder. The experiments were performed in open air. The sample was placed on a platinum ribbon and slowly heated to the desired temperature held for 20 min. The rate of heating was $20°\text{C} \cdot \text{min}^{-1}$. A 2θ angle range from 25° to 33° was

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chosen in order to observe the behaviour of (002) peak for the ZnO phase.

3. Results and discussion

The crystallinity of ZnO films deposited on Si (111) was investigated by XRD (Fig. 1). In the $\theta/2\theta$ scan curve (Fig. 1(a)), only diffraction peaks of ZnO (002) and (004) index planes appear in this curve, which proves that the film is strongly c-oriented. The lattice constant c of ZnO film is 5.168 Å calculated from the peak position of (002) plane using Bragg's law. This value is small in comparison with the bulk value of 5.205 Å. The difference in lattice parameter between ZnO film and the bulk is −0.118 Å, which indicates that the film is under compression stress along c direction. The stress is mainly caused by thermal mismatch between the ZnO epilayer and Si substrate.[13]

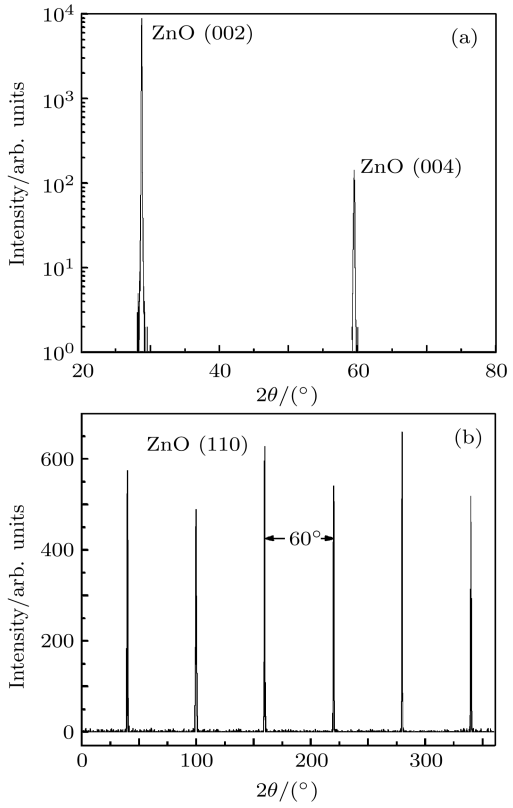


Fig. 1. The XRD spectra of the epitaxial ZnO thin film on Si (111) at room temperature: (a) $\theta/2\theta$ scan for ZnO thin film; (b) Phi-scan for ZnO (110).

The Phi-scan was employed to further analyse the in-plane orientation of the ZnO film relative to the Si substrate, as shown in Fig. 1(b). Six sharp Phi-scan peaks of the ZnO (110) at 60° intervals confirm that the epitaxial ZnO exhibits a single-domain wurtzite structure with hexagonal symmetry.

The full width at half maximum (FWHM) of the rocking curve indicates the crystal quality of the grown plane with higher precision than that obtained by the $\theta/2\theta$ scan method.[14] The FWHM of ZnO (002) plane as a function of temperature is shown in Fig. 2.

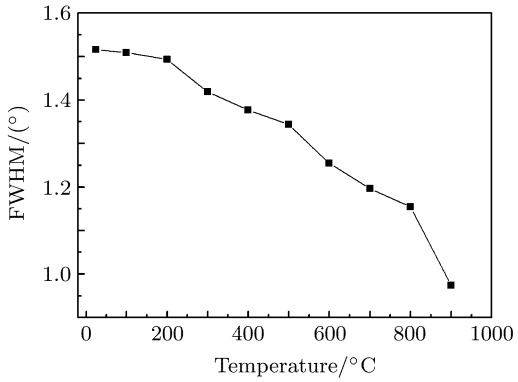


Fig. 2. The FWHM of ZnO (002) rocking curves at various temperatures.

It is observed that the FWHM of ZnO (002) plane rocking curves decreases from 1.52° to 0.97° with the temperature increasing from room temperature to 900°C. The decrease in the width of rocking curves suggests that high temperature removes defects in the ZnO crystals and improves their crystallinity.

The results of *in situ* high-temperature XRD in open air for ZnO thin film from 25°C to 900°C are shown in Fig. 3. It has been observed that the FWHM of XRD peak decreases with the increase of temperature. There is a gradual shift in the peak position towards lower 2θ values. It is well known that the lattice parameters are temperature-dependent, and an increase in temperature leads to expansion of the lattice.[15,16] It is observed that the particle size and lattice parameter of ZnO increase with increasing temperature as mentioned in Fig. 4. No phase change is observed in XRD pattern even after *in situ* heating of the film to 900°C.

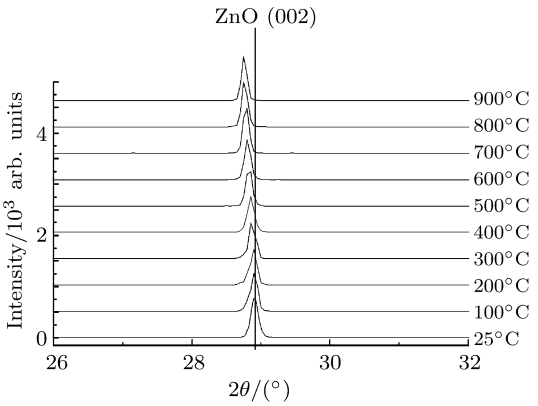


Fig. 3. The XRD spectra of ZnO thin film at various temperatures.

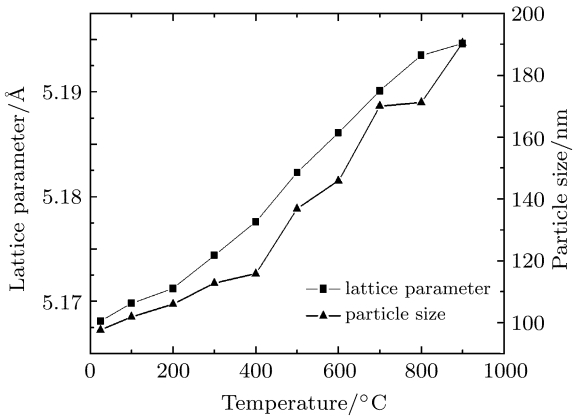


Fig. 4. Lattice parameter and particle size at various temperatures.

The XRD spectra were used to calculate the sizes of the ZnO nanoparticles with increasing temperature by using Scherrer's formula[17]

$$d = \frac{0.9\lambda}{B\cos\theta_{\rm B}},$$

where λ, $\theta_{\rm B}$ and B are the X-ray wavelength (1.29 Å), Bragg diffraction angle and FWHM after correcting the instrument peak broadening (B is expressed in radians) respectively. In order to measure the peak broadening of the instrument, we measured the FWHM of the instrument by ZnO single-crystal. As shown in Fig. 5, the FWHM of the peak (002) of ZnO single-crystal is 0.0422°, then subtract the FWHM of the instrument from the FWHM of ZnO thin film, and then substitute it into the Scherrer's formula.

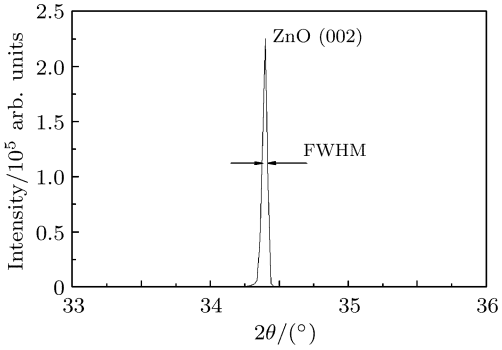


Fig. 5. The FWHM of the peak (002) of ZnO single crystal.

The lattice parameters and particle size as a function of temperature are shown in Fig. 4. It was found that the size of ZnO nanoparticles was around 97.7 nm at 25°C, which increased to 190.5 nm when the sample was heated to 900°C. According to Ostwald ripening, the increase in the particle size is due to the merging of the smaller particles into larger ones and is a result of potential energy difference between small and large particles and can occur through solid-state diffusion.[18,19]

4. Conclusions

In summary, an epitaxial ZnO thin film on Si (111) substrate was entirely fabricated by PLD. From the XRD analysis of ZnO thin film, we confirm that the resultant film is of pure ZnO with hexagonal (wurtzite) structure. High-temperature XRD also confirms that the ZnO thin film is stable not only at room temperature but also at high temperature (900°C). A linear increase in lattice parameters and the size of the grains are observed. An increment in crystallite size with the increase in temperature is attributed to the mergence of grain boundaries into neighbouring grains.

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