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Characterization of homoepitaxial and heteroepitaxial ZnO films grown by pulsed laser deposition

Z.Q. Chen[a,*], S. Yamamoto[a], A. Kawasuso[a], Y. Xu[a], T. Sekiguchi[b]

[a]Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan
[b]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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Abstract

Homo- and heteroepitaxial ZnO films were grown on ZnO (0 0 0 1) and Al_2O_3 $(1\,1\,\bar{2}\,0)$ substrates by using pulsed laser deposition. The X-ray diffraction and Raman measurements for these films show good correspondence with the bulk ZnO substrate, which confirms successful growth of *c*-axis oriented ZnO layer. Strong UV emission was also observed in these films, indicating good optical quality. However, the surface roughness differs very much for the homo- and heteroepitaxial film, that is, much less for the homoepitaxial layer. Positron annihilation measurements reveal a higher vacancy concentration in the homoepitaxial layer.

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Keywords: ZnO; Pulsed laser deposition; Film

1. Introduction

ZnO has been recognized as a promising material for the application in the short wavelength optoelectronic devices because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1]. It has also many other applications, such as the transparent conduction electrodes, promising substrate for GaN growth, and surface acoustic wave devices [2–4]. Growth of high quality ZnO films has become an intensive research field in recent years. Characterization of the structural, electric and optical properties of these films after growth is, therefore, a very important subject.

Pulsed laser deposition (PLD) method is very suited for the film growth, because it has the advantage of growing high quality films at relatively lower temperatures. In this work, we deposited ZnO thin

* Corresponding author. Tel.: +81 27 346 9330; fax: +81 27 346 9432.
E-mail address: chenzq@taka.jaeri.go.jp (Z.Q. Chen).

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films on the ZnO (0 0 0 1) and Al_2O_3 $(1 1 \bar{2} 0)$ substrates, respectively, and characterized these films by using different methods.

2. Experiment

A pulsed KrF excimer laser (248 nm, 10 Hz) was irradiated on a sintered bulk ZnO (purity 99.99%). ZnO films were deposited on the ZnO (0 0 0 1) and Al_2O_3 $(1 1 \bar{2} 0)$ substrates, respectively, at 500 °C. The oxygen partial pressure was about 10^{-2} Torr. The film thickness was 1–2 μm after 12 h deposition. The crystallinity of the films was evaluated by X-ray diffraction (XRD) using a high-resolution diffractometer (X'Pert-MRD, Philips). The surface morphology was probed by the atomic force microscope (AFM, Nanoscope IIIa). The Doppler broadening of positron annihilation radiation was measured using a slow positron beam to probe vacancy defects. The *S*-parameter was used to characterize the measured spectra. $S > 1$ indicates existence of vacancy defects [5]. Raman scattering measurements were also performed using the NANOFINDER spectrometer to check the lattice structure. The optical properties of the films were investigated by cathodoluminescence (CL) measurements using a scanning electron microscope (TOPCON DS130) attached with a beam blanking system.

3. Results and discussion

Fig. 1 shows the XRD patterns. For the homoepitaxial film, it shows only (0 0 0 2) and (0 0 0 4) peaks at 34.40 and 72.64°, respectively, which come from single crystalline ZnO. For the heteroepitaxial film, besides those ZnO peaks, there are also peaks from the Al_2O_3 substrate. The above results indicate that highly *c*-axis oriented ZnO films are successfully deposited on both the ZnO (0 0 0 1) and Al_2O_3 $(1 1 \bar{2} 0)$ substrates.

Fig. 2 shows the Raman spectra of the ZnO films grown on the Al_2O_3 and ZnO substrates, and also the bulk ZnO crystal. According to the selection rule of the phonon mode in the wurtzite structure of ZnO, the Raman active modes are: $A_1 + 2E_2 + E_1$, [6] where the E_2 mode represents the wurtzite structure. As shown in

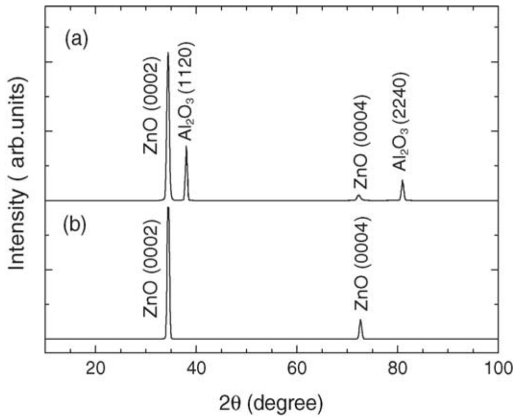

Fig. 1. X-ray diffraction patterns of the ZnO films grown on (a) Al_2O_3 and (b) ZnO substrates.

Fig. 2, for the ZnO single crystals, there is a dominant sharp peak at around 437 cm^{-1}, which is the high frequency E_2 mode. The peak at around 331 cm^{-1} is due to the second order phonon, and another small peak at around 575 cm^{-1} is induced by the intrinsic defects, most probably oxygen vacancies [7].

For both the PLD grown films, the dominant E_2 modes are clearly seen. Besides this E_2 mode, all the

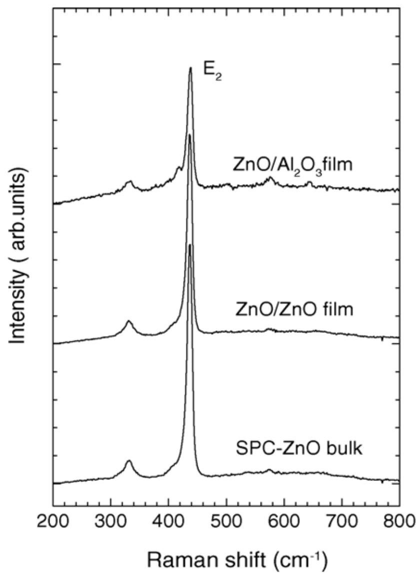

Fig. 2. Raman spectra of the ZnO films grown on the ZnO and Al_2O_3 substrates, together with the ZnO bulk crystals.

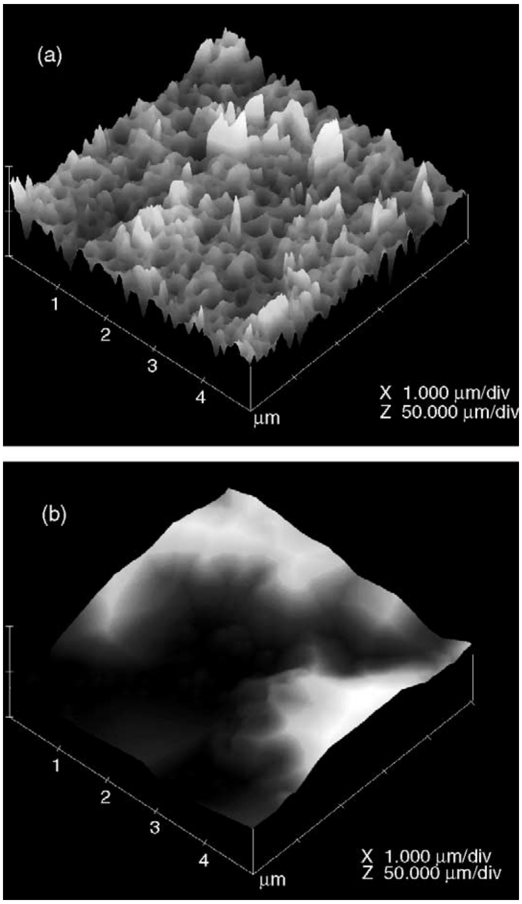

Fig. 3. AFM images of the surface of ZnO films grown on (a) ZnO and (b) Al_2O_3 substrates in the area of 5 μm × 5 μm. The *z*-axis scale is 50 nm/div and 1500 nm/div, respectively.

other peaks in the films also show correspondence with the bulk crystals. There are small peaks at 417 and 644 cm^{-1} in the heteroepitaxial film, which are from the Al_2O_3 substrate. Therefore, the Raman measurements also indicate successful growth of the ZnO wurtzite structure.

Fig. 3 shows the AFM images of the ZnO films. For the homoepitaxial film, the average surface roughness is about 6.7 nm in the scanned area of 5 μm × 5 μm with small grain size, indicating very smooth surface. While for the heteroepitaxial film grown on the Al_2O_3 substrate, it has an average roughness of 180 nm, and the lateral grain size is also very large. The surface roughness is only 1.1 nm for the Al_2O_3 substrate, and 4.1 nm for the ZnO substrate. These AFM results, thus

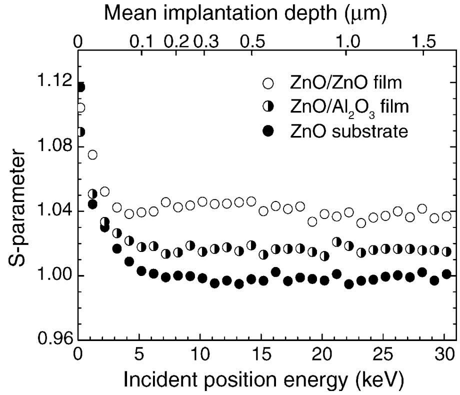

Fig. 4. Doppler broadening *S*-parameter as a function of incident positron energy in the ZnO films grown on the ZnO and Al_2O_3 substrates, together with the ZnO bulk crystals.

indicate that the surface morphology of the film depends strongly on the substrate materials.

Fig. 4 presents the Doppler broadening *S*-parameter as a function of positron incident energy for the ZnO films and the bulk single crystal. The *S*-parameter in the films are clearly higher than that of the vacancy free bulk crystal. This means the existence of vacancy-type defects in these films. In ZnO, the negatively

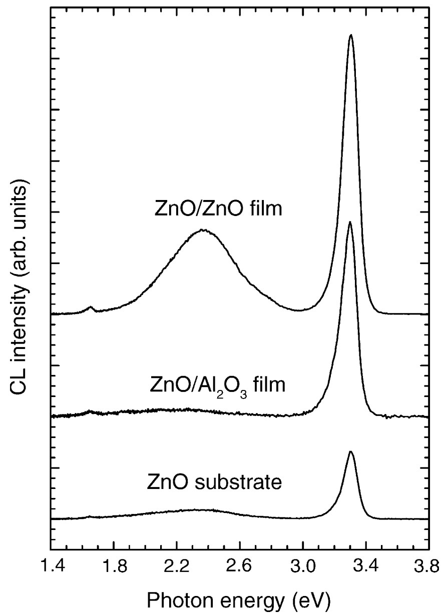

Fig. 5. Cathodoluminescence spectra of ZnO films grown on the ZnO and Al_2O_3 substrates together with the ZnO bulk crystal.

charged zinc vacancy (V_{Zn}) is the effective positron trapping center [8]. Gupta et al. [9] observed V_{Zn} in the grain boundary interface of the polycrystalline ZnO varistors using positron annihilation spectroscopy. These vacancies were found to be responsible for the electrically induced degradation of the varistors. Similarly, our results also indicate existence of V_{Zn}, possibly in the interface region between the small grains. The *S*-parameter in the homoepitaxial film is larger than that of the heteroepitaxial one, indicating higher concentration of defects due to the more grain boundary region. This is consistent with the AFM data, which shows much smaller grain size and much more grain boundary area in this homoepitaxial film.

Cathodoluminescence spectra in these films show two emission peaks, as indicated in Fig. 5. The band edge ultraviolet (UV) emission at around 3.3 eV is from the free exciton recombination, while the green emission at around 2.3 eV is due to deep level defect centers [10]. The UV emission peaks in all the films are much higher than that of the bulk crystals, indicating better optical quality. The deep level emission in the heteroepitaxial film is very weak, however, this peak is rather high in the homoepitaxial film. This suggests large number of defects in the ZnO/ZnO film. The positron annihilation measurements also show higher concentration of vacancy-type defects in the homoepitaxial film. However, the origin of the deep level defects responsible for the green emission is still under debate [11,12], it is difficult to determine whether these deep level defects observed by CL measurements are related with the positron detected vacancies. Further experiments are needed to clarify the relationship between these defects.

4. Conclusion

ZnO films are grown on the ZnO (0 0 0 1) and Al_2O_3 $(1\,1\,\bar{2}\,0)$ substrates using PLD technique. XRD and Raman measurements show good *c*-axis oriented ZnO films. The surface roughness detected by AFM strongly depends on the substrate materials, which is much smaller in the homoepitaxial layer. Positron annihilation measurements indicate large number of vacancy defects in the ZnO/ZnO films, which probably come from the grain boundary region. All the films show strong UV emission, indicating superior optical properties.

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