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Structural and optical properties of epitaxial ZnO thin films on 4H–SiC (0 0 0 1) substrates prepared by pulsed laser deposition

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ABSTRACT

Epitaxially grown ZnO thin films on 4H–SiC (0 0 0 1) substrates were prepared by using a pulsed laser deposition (PLD) technique at various substrate temperatures from room temperature to 600 °C. The crystallinity, in-plane relationship, surface morphology and optical properties of the ZnO films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL) measurements, respectively. XRD analysis showed that highly *c*-axis oriented ZnO films were grown epitaxially on 4H–SiC (0 0 0 1) with no lattice rotation at all substrate temperatures, unlike on other hexagonal-structured substrates, due to the very small lattice mismatch between ZnO and 4H–SiC of ~5.49%. Further characterization showed that the substrate temperature has a great influence on the properties of the ZnO films on 4H–SiC substrates. The crystalline quality of the films was improved, and surfaces became denser and smoother as the substrate temperature increased. The temperature-dependent PL measurements revealed the strong near-band-edge (NBE) ultraviolet (UV) emission and the weak deep-level (DL) blue-green band emission at a substrate temperature of 400 °C.

1. Introduction

As a II–VI compound semiconductor with a hexagonal wurtzite structure, ZnO has attracted much attention because of its attractive electrical and optical properties which are useful in various applications such as light-emitting diodes, photodetectors, thin film transistors and transparent electrodes [1–3]. Above all, ZnO films can be used to produce optoelectronic devices operating in the ultraviolet (UV) spectral region due to its direct wide band gap (E_g) of ~3.37 eV and large exciton binding energy (~60 meV). In this application, the ZnO film with high crystalline quality is preferred for the fabrication of high-performance devices [4–6]. In this regard, the choice of the substrate is very important since it affects the epitaxial growth of ZnO. Also, the role of the substrate is principal for the achievement of nonlinear optical effects [7]. So far, hexagonal-structured substrates such as Al_2O_3, $LiNbO_3$ and SiC have been used to grow high quality epitaxial ZnO thin films [8–15]. Among these, SiC has the smallest lattice mismatch to ZnO. Moreover, unlike other insulating substrates, SiC can form hetero-junction semiconductor devices with ZnO. Recently, there have been several reports on ZnO/6H–SiC hetero-structures fabrication and characterization [12–14]. Among the many polytypes of SiC, 4H–SiC is considered as the most attractive for device applications due to its wider band gap (~3.2 eV), and higher and more isotropic mobility than the other polytypes. However, relative to work carried out with 6H–SiC substrates, little effort has been spent on attempts to grow epitaxial ZnO films on 4H–SiC [15]. Furthermore, to our knowledge, no report has specifically examined the in-plane relationship of epitaxial ZnO thin films to 4H–SiC (0 0 0 1) substrates and its optical properties.

In this work, we report successful epitaxial growth of ZnO thin films on 4H–SiC (0 0 0 1) substrates by pulsed laser deposition (PLD). The PLD technique is very useful for the preparation of high quality ZnO films at lower temperature due to the high energy of the ablated particles [16]. The deposition was carried out at various substrate temperatures from room temperature to 600 °C. X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL) measurements were made to investigate the

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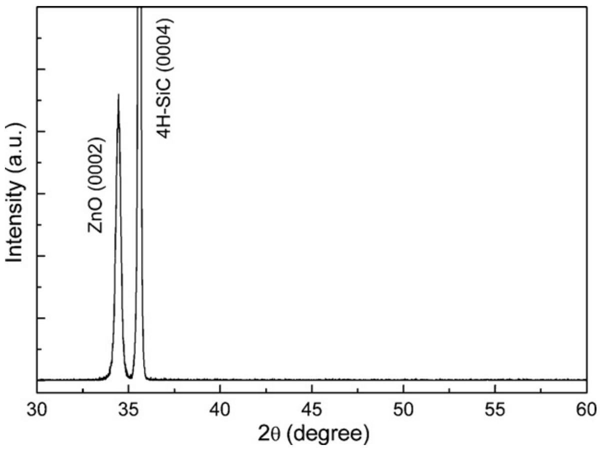

Fig. 1. XRD θ–2θ pattern of the ZnO thin films on 4H–SiC substrates.

crystallinity, in-plane relationship, surface morphology and optical properties of the deposited films.

2. Experimental

ZnO thin films were deposited on 4H–SiC (0 0 0 1) substrates by using a PLD system. A Q-switched Nd:YAG laser (Continnum, Surelite III) with a wavelength of 355 nm was used to ablate a ZnO ceramic target (99.999%). The distance between the target and the substrate holder was fixed at 50 mm. In view of the importance of low temperature deposition for device applications, the substrate temperature was limited to between room temperature and 600 °C. The deposition was carried out for 10 min in an oxygen partial pressure of 30 mTorr, which resulted in $\sim$300 nm-thick ZnO films. The crystalline properties of the films were examined using a high resolution X-ray diffractometer (HRXRD, Philips, X'pert PRO MRD) with CuKα radiation. The diffracted intensities were collected in θ–2θ scan and ω-rocking curve scan modes. In addition, the pole figure measurements were carried out in order to study the in-plane relationship between the ZnO films and 4H–SiC substrates. An atomic force microscope (S.I.S., PICOStation) was used to observe the surface morphology of the films. The optical properties of the films were investigated by PL measurements at room temperature using a He–Cd laser with a wavelength of 325 nm (Kimmon, IK series).

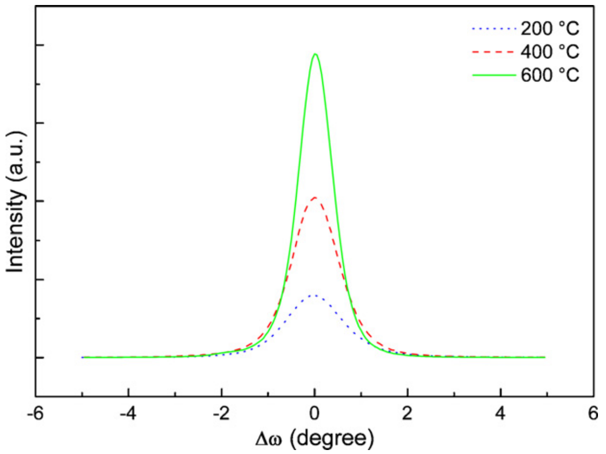

Fig. 2. XRD ω-rocking curve patterns for ZnO (0 0 0 2) diffraction at different substrate temperatures.

3. Results and discussion

Fig. 1 shows the XRD θ–2θ patterns of the ZnO thin films on 4H–SiC (0 0 0 1) substrates. The reflection from ZnO (0 0 0 2) and 4H–SiC (0 0 0 4) plane appear at around 34.4° and 35.6°, respectively. These peaks imply that the ZnO films were grown along the *c*-axis on 4H–SiC (0 0 0 1) substrates due to the lowest surface free energy of the close-packed (0 0 0 2) plane in the ZnO crystal [17]. The crystalline quality was further determined by XRD ω-rocking curve measurements of ZnO (0 0 0 2) diffraction, as shown in Fig. 2. As the substrate temperature increases, the ZnO (0 0 0 2)

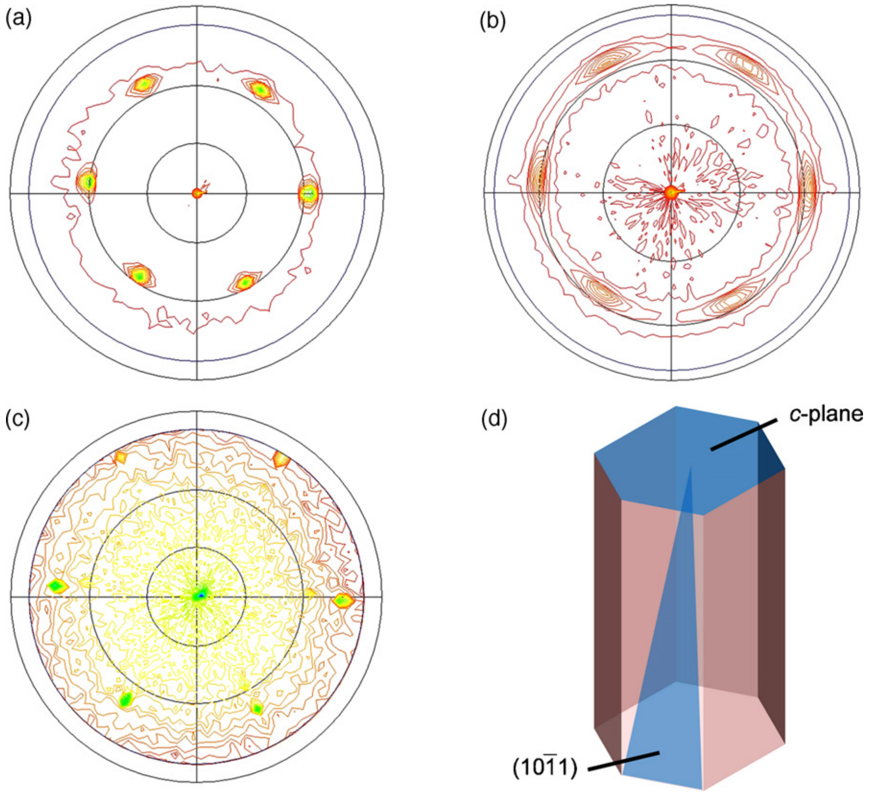

Fig. 3. XRD pole figures of (a) ZnO (10$\bar{1}$1) at 400 °C, (b) ZnO (10$\bar{1}$1) at room temperature and (c) 4H–SiC (10$\bar{1}$1). (d) Schematic of the hexagonal unit cell.

peak becomes sharper and stronger. The full width at half maximum (FWHM) values of the ZnO (0 0 0 2) peaks from the films deposited at 200 °C, 400 °C and 600 °C are 1.4366°, 1.2096° and 0.8773°, respectively, which clearly indicates that the crystalline quality of the films improves with increasing substrate temperature.

The in-plane relationship between the ZnO films and 4H–SiC (0 0 0 1) was determined by XRD pole figure measurements. Fig. 3(a) and (b) presents a comparison of pole figures at $2\theta = 36.25°$ corresponding to ZnO $(10\bar{1}1)$ deposited at 400 °C and room temperature, respectively. The $(10\bar{1}1)$ plane in the hexagonal structure can be seen in Fig. 3(d). In Fig. 3(a), the six symmetrical poles separated by 60° (φ) and the central pole from 4H–SiC (0 0 0 4) are observed, which confirmed the epitaxial growth of the ZnO film. Fig. 3(b) shows pole figure patterns of the ZnO $(10\bar{1}1)$ deposited at room temperature. The sixfold symmetry implies that the epitaxial ZnO film could be obtained even at room temperature. However, the poles are broad and weak, which is attributed to the poor crystalline quality than at 400 °C. These results are consistent with the tendency that was confirmed by the previously shown XRD ω-rocking curve measurements.

The orientational relationship between the ZnO films and 4H–SiC (0 0 0 1) can be understood by comparing the results with Fig. 3(c), which shows the pole figure of 4H–SiC $(10\bar{1}1)$ at $2\theta = 34.08°$. The six symmetrical poles corresponding to 4H–SiC $(10\bar{1}1)$ appear on the same φ-angles of the previously shown ZnO $(10\bar{1}1)$ pole figure. The central pole is attributed to ZnO (0 0 0 4). These results imply that the ZnO thin films were epitaxially grown on 4H–SiC (0 0 0 1) with no-rotation of a single cell with respect to that of 4H–SiC. So, the in-plane orientation relationship between the ZnO thin film and 4H–SiC (0 0 0 1) substrate is ZnO $[11\bar{2}0]\|$4H–SiC $[11\bar{2}0]$. Previous reports showed that ZnO thin films can be grown epitaxially on various hexagonal-structured substrates with a 30°-rotation of unit cell; ZnO $[11\bar{2}0]\|$substrate $[01\bar{1}0]$ [8–11]. For example, Chen et al. have reported that a 30°-rotated ZnO epilayer was grown on c-Al_2O_3 to reduce the lattice mismatch from around 32% to 18% [9]. Furthermore, Zhang et al. have shown that the orientational relationship between ZnO and c-Al_2O_3 is strongly dependent on the substrate temperature [10]. In the case of a c-$LiNbO_3$ substrate which has also hexagonal structure, 30°-rotation between ZnO and $LiNbO_3$, similar to the case of ZnO on c-Al_2O_3, has been demonstrated by Matsubara et al. Owing to this rotation, the lattice mismatch between ZnO and $LiNbO_3$ is 9.3% which is smaller than that between ZnO and c-Al_2O_3 [11]. However, in our work, there was no-rotation of ZnO at any of the substrate temperatures employed because of the very small lattice mismatch between ZnO and 4H–SiC. The lattice mismatch is defined as

$$\varepsilon_{\text{lattice}} = (a_{\text{sub}} - a_{\text{ZnO}})/a_{\text{sub}},$$

where a_{sub} and a_{ZnO} are the lattice constants of the substrate and ZnO, respectively. The calculated lattice mismatch between ZnO and 4H–SiC using $a_{\text{ZnO}} = 3.249$ Å and $a_{\text{4H–SiC}} = 3.08$ Å is about 5.49% with no-rotation of the ZnO unit cell. It is a very small value compared to 18% with c-Al_2O_3 and 9.3% with c-$LiNbO_3$. The in-plane relationships between the ZnO thin films and several hexagonal-structured substrates are illustrated in Fig. 4.

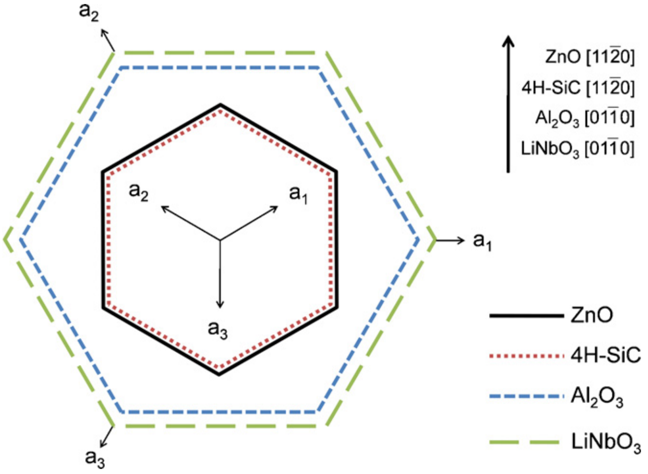

Fig. 4. Schematic diagram of in-plane relationships between ZnO and several hexagonal-structured substrates.

Fig. 5 shows the AFM images of the ZnO films deposited at 200 °C, 400 °C and 600 °C on 4H–SiC substrates. The scan area is 1 μm × 1 μm in each scan. It can be seen that the surface of the ZnO films becomes relatively denser and smoother as the substrate temperature increases. The root-mean-square (rms) values of surface roughness are 3.82 nm, 2.23 nm and 1.16 nm at 200 °C, 400 °C and 600 °C, respectively. These results indicate that the surface of the ZnO films becomes relatively denser and smoother as the substrate temperature increases. Thus, it is clear that the substrate temperature has a great influence not only on the crystalline quality but also on the surface morphology of the ZnO films on 4H–SiC substrates.

The PL spectra of the ZnO films are shown in Fig. 6. It has been proposed that the near-band-edge (NBE) ultraviolet (UV) emission at around 380 nm is attributed to the recombination of free excitons. Also, and the deep-level (DL) blue-green band emission centered around 510 nm is due to oxygen vacancies and interstitial zinc [18]. In our research, NBE emission with broad DL emission was observed. At a substrate temperature of 400 °C, the strongest NBE emission and weak DL emission were obtained, which suggests that the ZnO film is more stoichiometric than any other deposited film. At a substrate temperature of 200 °C, NBE emission is very

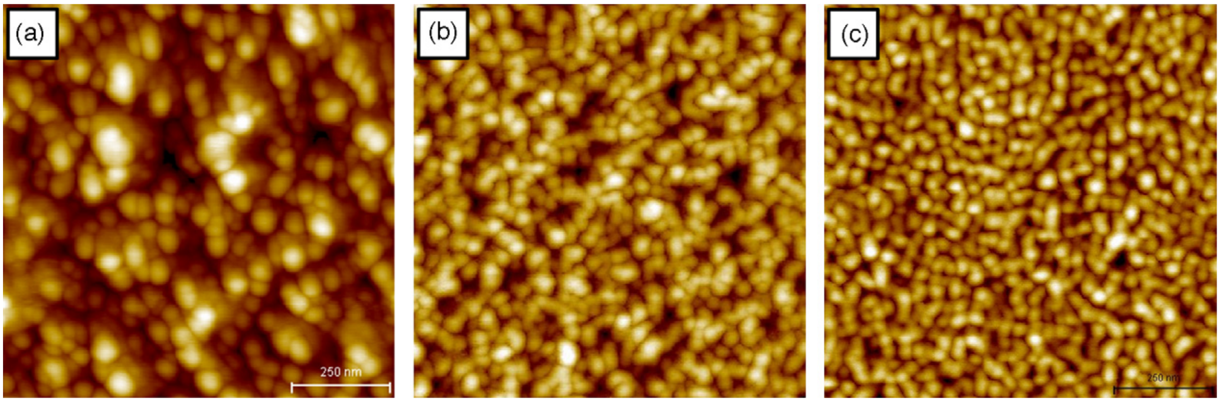

Fig. 5. AFM images of the ZnO thin films deposited at (a) 200 °C, (b) 400 °C, and (c) 600 °C.

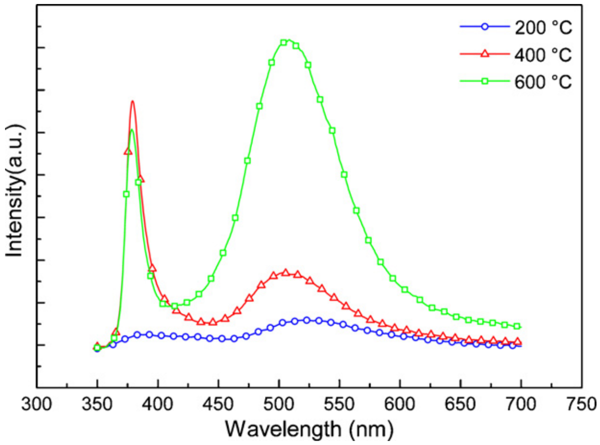

Fig. 6. PL spectra of the ZnO thin films deposited at different temperatures.

weak owing to low energy to form stoichiometric ZnO films. When the substrate temperature is 600 °C, Zn evaporation due to high temperature results in inferior stoichiometric ZnO films and as a result, NBE emission is weaker and DL emission stronger than those of the ZnO films deposited at 400 °C [19]. The increase of the DL emission peak with higher substrate temperature can be explained by the formation of point defects including oxygen vacancies. The defects could be reduced by several methods reported by other researchers such as the post-annealing and variation of the film thickness [20,21]. According to these results, it could be considered that the PL characteristics of the ZnO films on 4H–SiC substrates are closely related to the substrate temperature as well as to the crystallinity and surface morphology.

4. Conclusions

ZnO thin films were epitaxially grown on 4H–SiC (0 0 0 1) substrates using PLD with a range of substrate temperatures from room temperature to 600 °C. The improvement of the crystalline quality, and denser and smoother surface of the films with increasing substrate temperature were observed by XRD ω-rocking curve measurement and AFM. The pole figure measurements at $2\theta = 36.25^\circ$ corresponding to ZnO $(10\bar{1}1)$ showed the six symmetrical poles being separated by 60° (φ). These results were indicative of the epitaxial growth of ZnO on 4H–SiC (0 0 0 1) substrates. In addition, there was no-rotation of the ZnO single cell with respect to that of 4H–SiC at all substrate temperatures unlike the case with other hexagonal-structured substrates such as Al_2O_3 and $LiNbO_3$. PL spectra showed NBE emission and broad DL emission, which were strongly related to the substrate temperature. These results may serve as a basis for realizing ZnO/4H–SiC hetero-junction semiconductor devices.

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