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Growth and characterization of device quality ZnO on Si(111) and c-sapphire using a conventional rf magnetron sputtering

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Abstract In this article, it is shown that high quality ZnO films were grown on Si(111) and $Al_2O_3(0001)$ substrates using a conventional rf magnetron sputtering. High-resolution X-ray diffractometry (HR-XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and photoluminescence (PL) investigations clearly confirmed that the ZnO films grown on Al_2O_3 (0001) at substrate temperatures above 650°C are single crystal as well as high optical quality. It is also estimated in both cases grown on Si and Al_2O_3 that an introduction of template pre-grown at 500°C can induce a homogeneous interface and improvement of emission characteristic by relaxing the strain caused by large lattice and thermal mismatch between the film and substrate and by reducing defect density in interface region.

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1 Introduction

Currently, ZnO is attracting much attention for its application to ultra-violet (UV) and blue light-emitting opto-electronic devices and it has advantages relative to GaN owing to its availability in bulk, single-crystal form and its larger exciton binding energy (∼60 meV, ∼25 meV for GaN) to assure more efficient exciton emission even at high temperatures above room temperature [1,2].

For device application, the growth of high quality ZnO with a smooth surface morphology and a high crystalline ordering as well as high emission efficiency is essential to assure a high performance and a long lifetime of device. However, growth of single crystal ZnO films has been mainly achieved on Al_2O_3 in sophisticated and finely controlled thin film growth techniques such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) [3–6]. Despite the epitaxial growth of high quality ZnO using these methods, they might have disadvantage in mass production, due to high cost and low throughput. While it would be very desirable to be able to grow high quality single crystal ZnO films using the sputter technique in terms of large area deposition and low cost. In addition, from the viewpoint of hybridization with Si-based LSI structure, the growth of high quality ZnO on Si is also of much valuable.

In this study, we have tried to prepare high quality ZnO films on Si(111) and $Al_2O_3(0001)$ substrates using a conventional rf magnetron sputtering. Influence of low-temperature (LT) grown template on the resultant film quality has been also evaluated.

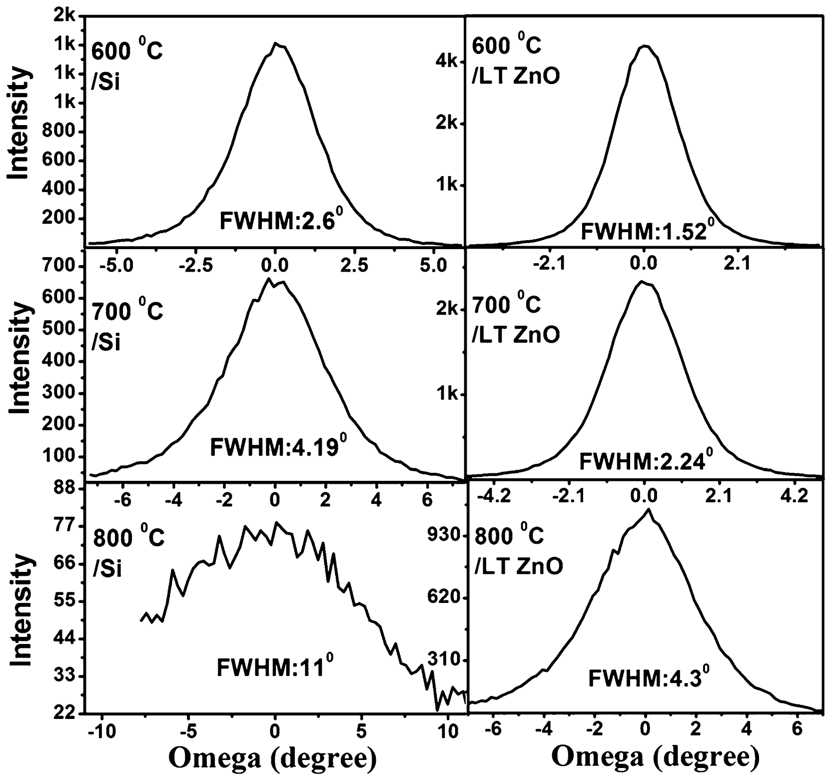


Fig. 1 ω-rocking curves for the ZnO (0002) diffraction peak of the films grown directly on Si and on LT ZnO/Si at growth temperatures in the range from 600 to 800°C

2 Experimental procedure

Hetero-epitaxial ZnO films were grown on c-plane Al_2O_3 (0001) and Si (111) substrates by sputtering from a 2 inches in diameter ZnO target (99.999%) using an rf magnetron sputter system. Film growth was carried out in pure oxygen at a constant working pressure of 1×10^{-2} torr and an rf power of 75 Watt, which is optimized condition from our previous studies [7–8]. The substrate temperature in the range of 600–800°C was adopted as a variable, during film growth. For investigating the effects of LT-grown template, pre-growth of the under-lying ZnO layer with a thickness of about 50 nm was performed at 500°C, prior to the growth of the main ZnO layer. All of films had a thickness of about 1 μm.

Crystallinity and orientation of the prepared ZnO layers were assessed with the Philips X′Pert PRO-MRD high-resolution 4-crystal triple axis X-ray diffractometer (HR-XRD), using a Cu Kα radiation. The photoluminescence (PL) spectra were obtained at 12 K and room temperature using a closed-cycle liquid helium cryogenerator (APD, SH-4, USA), a spectrometer ($f = 0.5$ m, Acton Research Co., Spectrograph 500i, USA), and an intensified photo diode array detector (Princeton Instrument Co., IRY1024, USA). A He-Cd laser (Kimon, 1 K, Japan) with a wavelength of 325 nm and a power of 50 mW was utilized as an excitation light source. A JEOL JEM 2000 FX transmission electron microscope (TEM), a scanning electron microscope (SEM) (Hitachi, S-4700), and a Digital Instruments Multimode atomic force microscope (AFM) were also employed to observe the microstructure of the samples.

3 Results and discussion

3.1 ZnO/Si(111)

Crystallinity of the ZnO/Si(111) films with and without LT-grown template prepared at growth temperatures in the range of 600–800°C was evaluated by XRD measurements using a θ-2θ scan and ω-scan. XRD patterns measured by a θ-2θ scan mode (data not shown) indicated that all the films are highly c-axis oriented, showing only XRD peaks corresponding to the hexagonal (000l) ZnO phase except the diffraction peaks originating from Si substrate. The ω-rocking curves for the ZnO (0002) diffraction peak and their FWHM values are seen in Fig. 1. The FWHM of ZnO (0002) peak increases gradually with growth temperature in both cases with and without template layer, indicating the enhancement of mis-orientation in plane during growth at high temperature. Even though the detailed growth mechanism depending on the growth temperature cannot be understood explicitly, it is considered that the increase in mis-orientation at high growth temperature may be due to a large lattice mismatch and a large difference in thermal expansion coefficients

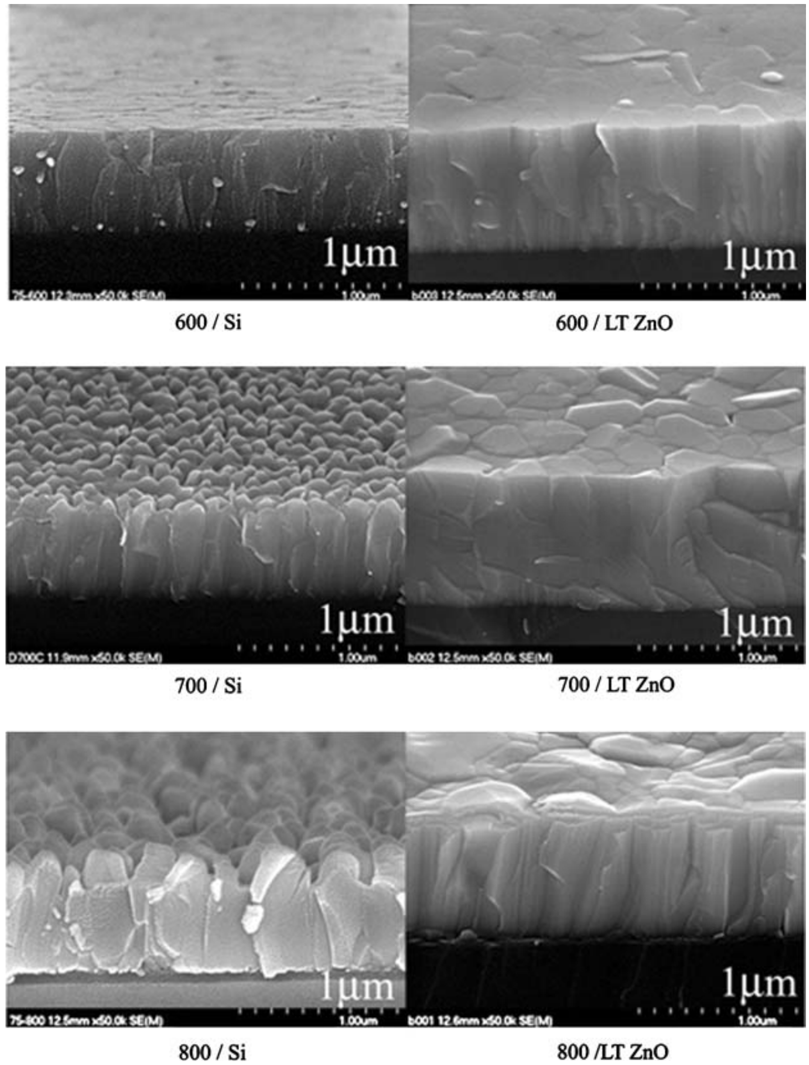


Fig. 2 SEM images for the ZnO films grown directly on Si and on LT ZnO/Si at growth temperatures in the range from 600 to 800°C

between ZnO and Si substrate. Noticeably, ZnO layers with LT-grown template show (0002) rocking-curves with a narrower FWHM and more symmetric shape, compared with those without LT-grown template, which means the improvement of crystal quality and the relaxation of strain in the interfacial region.

Figure 2 shows the SEM images for the same samples. In photographs, the surface morphology becomes more roughened with the growth temperature increasing from 600 to 800°C, on the contrary, when the film grows on LT-grown template, more lateral growth occurs and this change in growth mode results in more flat film.

From the above XRD and SEM results, it is suggested that pre-grown ZnO layer can serve as a good template during ZnO growth on Si at high temperature, causing the significant improvement of structural quality. These improvements induced by an introduction of template layer can be explained by following mechanisms; Firstly, pre-grown ZnO template creates an adhesive surface and provides nucleation sites for the subsequent high-temperature ZnO growth. Second, holding in-plane information of the under-layered crystals and the relaxation and re-crystallization of the ZnO lattice during post-deposition at high temperatures would play a key role in the improvement of the crystal quality of the over-grown ZnO layer at high temperature [9].

Figure 3(a) shows the room temperature PL spectra for the three samples grown directly on Si at 600 and 800°C and on LT template at 800°C. In the PL spectra, the typical emissions composed of narrow exciton related ultra-violet (UV) band peaked at 375 nm and broad defect related visible band are observed and intensities of emission peaks are strongly dependent on growth temperature, showing a sharp increase in intensity of both peaks with increasing growth temperature. This behavior of PL peaks can be attributable to the increase of the grain size in film when the film grows at high temperature, as seen in Fig. 2. A notable difference between the films grown directly on Si and on template is also clear in spectra. In the PL spectra of the film on template,

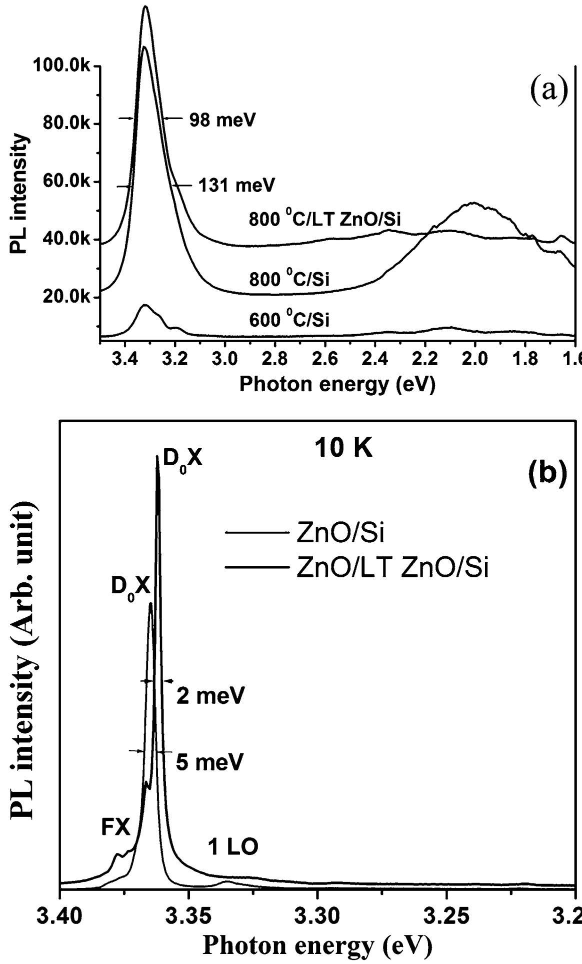


Fig. 3 (a) Room temperature PL spectra of three samples grown directly on Si at 600 and 800°C and on LT ZnO/Si at 800°C and (b) low temperature PL spectra (10 K) in high energy region taken at high resolution mode from two ZnO films grown directly on Si and on LT ZnO/Si at 800°C

the visible emission band is remarkably suppressed without reduction of band-edge emission and the FWHM of band-edge emission is further narrow, when compared with PL spectra of the film directly grown on Si. This improvement of optical quality may be due to the higher structural quality as demonstrated in the XRD and SEM results, because less deformed interface and higher crystalline ordering can result in a lower concentration of defect in both the interface and bulk regions.

Figure 3(b) shows LT PL spectra obtained in the range from 3.2 eV to 3.4 eV using high resolution (HR) mode for two ZnO films grown directly on Si and on template/Si at 800°C. Remarkable differences are apparent in two spectra. Only donor-bound exciton (D_oX) peak at 3.365 eV is observable in the PL spectrum of the ZnO film without template, on the contrary the free exciton (FX) peak at 3.378 eV besides the D_oX peaks at 3.362 eVand 3.366 eV is clearly discernable in the PL spectrum of the ZnO film with template. In commonly fabricated ZnO films and bulk crystals, free exciton emission is rarely observed at low temperatures because of the localization of excitons by impurities or defects, especially by donors. Therefore, the appearance of FX peak in the emission spectra of the ZnO film with template further supports a high purity of the film and the low defect concentration in film. In addition, the FWHM of D_oX emission at 3.362 eV in the emission spectra of the ZnO film on template is as narrow as 2 meV and this value is rather smaller than the value, 3 meV reported for the MBE grown ZnO single crystal film on sapphire [10].

3.2 ZnO/Al_2O_3(0001)

ZnO/Al_2O_3(0001) films with and without LT-grown template have been prepared at growth temperatures of 650°C and 800°C. XRD spectra of these films (data not shown) measured by θ-2θ scan showed only three peaks corresponding to ZnO(0002), ZnO(0004), and Al_2O_3(0006) planes, indicating an epitaxial relationship, $(0001)_{ZnO} \| (0001)_{Sapphire}$. Evidences for single crystalline nature of these films were obtained from XRD, TEM, SEM and AFM investigations.

Figure 4 shows a typical (a) X-ray pole figure, (b) cross-sectional TEM diffraction pattern, and (c) SEM image for ZnO/c-sapphire film grown at 800°C. In X-ray pole figure pattern (Fig. 4(a)) recorded from the ZnO $(10\bar{1}1)$ reflection (36.28°), the six poles, separated one from

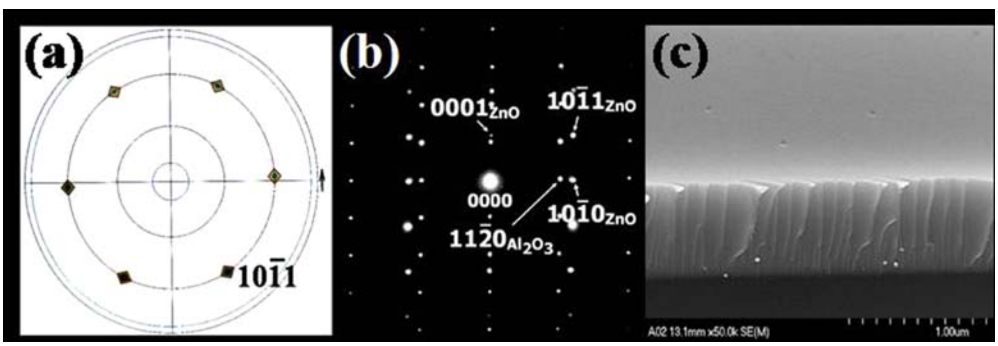


Fig. 4 Typical (a) X-ray pole figure, (b) cross-sectional TEM diffraction pattern, and (c) SEM image for ZnO/c-sapphire film grown at 800°C

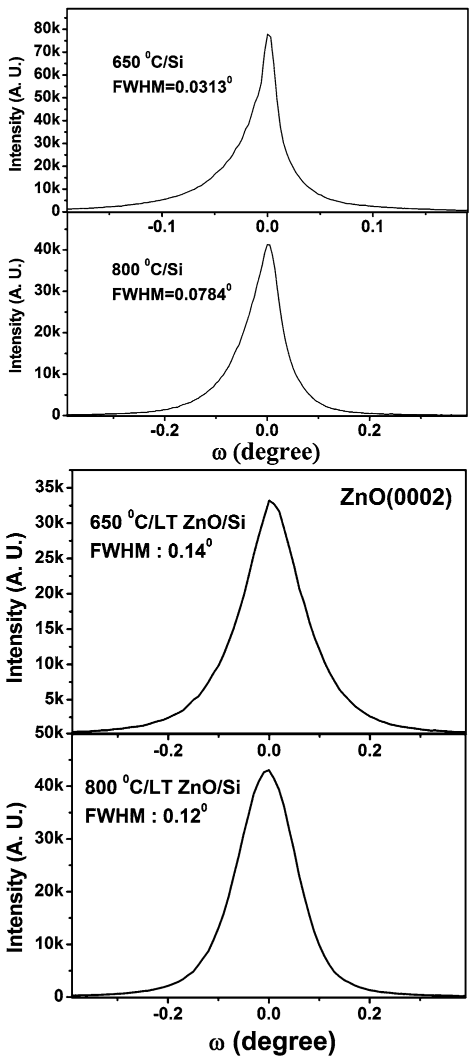


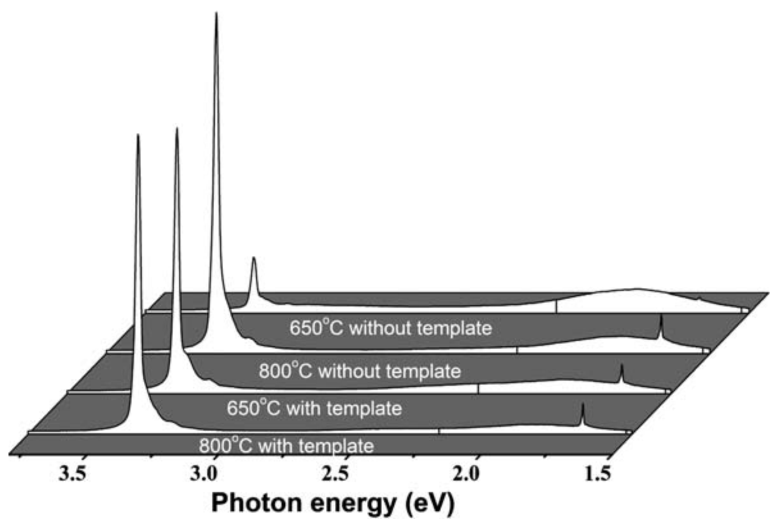
Fig. 5 ZnO (0002) ω-rocking curves and their FWHMs for the $ZnO/Al_2O_3(0001)$ films with and without LT template grown at temperatures of 650 and 800°C

another by 60°, are evident and this rotational symmetry clearly indicates the homogeneous in-plane alignment of the grown ZnO layer. In Fig. 4(b), by indexing diffraction patterns, the epitaxial relationship of the film is determined to be $ZnO[01\bar{1}0]//Al_2O_3[\bar{1}2\bar{1}0]$ and $ZnO[0001]//Al_2O_3[0001]$. This orientational relationship is consistent with that previously reported from the MOCVD or MBE grown ZnO/Al_2O_3 (0001) films and corresponds to 30° rotation of the film with respective to the substrate [11,12]. No noticeable features are also observed in the SEM image (Fig. 4(c)), along with AFM root mean square (RMS) roughness of about 0.2 nm (data not shown), which means an extremely flat surface. These observations clearly demonstrate that this film is single crystal.

It is also observed in Fig. 5 that with an insertion of LT template between film and substrate, The ZnO (0002) ω-rocking curves become slightly broader, on the contrast, the shape of curve changes to more symmetric pattern in comparison with those for the films without template at same temperatures, which may indicate less strained and deformed interfacial region [10]. The above observation may suggest that even though the LT template cannot contribute to the improvement of crystal quality of the over-grown ZnO layer at high temperature due to its relatively poor crystal quality, it plays a major role in relaxing the strain induced by the large lattice and thermal mismatch between the ZnO and Al_2O_3.

Figure 6 shows 12 K PL spectra of the ZnO films with and without LT template grown at 650 and 800°C. The sharp and strong UV emission peak at 3.368 eV is dominant in all spectra, which is assignable to the exciton transition bound to neutral donor. A noticeable difference in emission characteristic is found. In the PL spectra of the film without template, the visible emission band centered near 1.9 eV is observable, whereas this emission band is fully suppressed in the PL spectrum of the films with template, implying the improved optical quality. Especially, this trend is further obvious in the case of the films grown at 650°C. This difference in emission

Fig. 6 Low temperature (12 K) PL spectra of the $ZnO/Al_2O_3(0001)$ films with and without LT template grown at 650 and 800°C



characteristic can be considered to have a close relation with the strained and deformed interface region, as indicated by ω-rocking curves in Fig. 5 because the highly strained and deformed interface region can include a higher concentration of defects.

4 Conclusions

In summary, we have tried to prepare high quality ZnO films on Si(111) and Al_2O_3(0001) substrates using a conventional rf magnetron sputtering. From various structural and optical characterizations, it has been shown that high quality ZnO films with a single crystalline nature were successfully grown on Al_2O_3 substrates and with an introduction of LT grown template, significant improvement of both the optical and structural quality could be also achieved for the ZnO films grown on Si and c-plane sapphire.

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