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Crack-Free Epitaxial ZnO film on Si(111) with $Gd_2O_3(Ga_2O_3)$ buffer layer

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1. Introduction

Wurtzite-structure ZnO is a II–VI semiconductor with a wide direct band gap of 3.37 eV. One of the most attractive features of ZnO is the large exciton binding energy (60 meV), which is almost three times higher than that of GaN (25 meV). Much attention has been paid to heteroepitaxially grown ZnO on Si substrate, because of low costs, excellent quality, large-area availability of Si wafer, and unique possibility of integrating well-established Si electronics with ZnO-based optoelectronic devices. However, direct growth of ZnO on Si usually results in polycrystalline or textured films due to the formation of amorphous oxide on the Si surface. The other troublesome issue for the growth of ZnO epi-films on Si is the existence of cracks originating from the large mismatch in lattice (-15.4%) and thermal expansion coefficient between ZnO ($\alpha_a = 6.5\times10^{-6}\mathrm{K}^{-1}$) and Si ($\alpha_a = 3.6\times10^{-6}\mathrm{K}^{-1}$). Both mismatches could lead to the significant tensile stress and the formation of cracks. Although significant efforts have been made to use various materials, such as Y_2O_3, γ-Al_2O_3 , Lu_2O_3 and Sc_2O_3, as buffer layers [1-4], the growth of high-quality and crack-free ZnO epi-films on Si is still regarded as a difficult task. In many cases, cracks are already observed in ZnO epi-layers of thickness as thin as 300-600 nm.

In this letter, we report the growth of crack-free epitaxial ZnO films on Si (111) substrates buffered with $Gd_2O_3(Ga_2O_3)$ (GGO). The structural properties of ZnO/GGO/Si(111) hetero-epitaxial system was thoroughly examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Superior optical characteristics of the ZnO films were verified by photoluminescence (PL) at room temperature (RT) and low temperature (LT).

2. Experimental

Si (111) wafers were initially cleaned with the Radio Corporation America (RCA) method followed by HF acid dip for 20 sec. before loading into the growth chamber. A 9 nm thick GGO buffer layer with the cubic bixbyite structure was deposited by molecular beam epitaxy (MBE). The composite substrate was then transferred through air exposure into the pulsed laser deposition (PLD) chamber. The beam out of a KrF excimer laser (λ = 248 nm) was focused to produce an energy density ～5-7 cm^{-2} on a commercial hot-pressed stoichiometric ZnO (5N) target at a repetition rate of 10 Hz. ZnO was deposited at substrate temperature ranging from 200 to 500°C without introducing oxygen gas and the growth rate was ~0.48 $\mathrm{Ås}^{-1}$. ZnO layers with thickness up to 700 nm were studied and no cracks were found in all the samples. The data presented in this work are taken from the sample with a ~ 700 nm thick ZnO layer. X-ray measurements were conducted using a four-circle diffractometer at beamline BL13A of National Synchrotron Radiation Research Center (NSRRC) with an incident wavelength 1.0247 Å. Cross sectional TEM specimens with the thickness of about 90 nm were prepared by focused ion beam (FIB). TEM images were taken with a Philips TECNAI-20 field emission gun type TEM. PL measurements were carried out using a He-Cd laser with wavelength of 325 nm as the pumping source. The emitted light was dispersed by a Triax-320 spectrometer and detected by an UV-sensitive photomultiplier tube.

3. Results and Discussion

A radial scan along the surface normal (θ–2θ scan) of the ZnO layer grown at 400°C is illustrated in Fig. 1(a). Only ZnO (0002), (0004) and (0006) reflections were observed together with the Si (nnn), where n = 1, 2, and 3, reflections, elucidating the crystalline orientation of $(0002)_{ZnO} \parallel (111)_{Si}$ along the surface normal. Azimuthal cone scans (ϕ-scans) across the off-normal ZnO $\{10\bar{1}1\}$, GGO {440}, GGO {400} and Si {220} reflections, as illustrated in figure 1(b), were performed to examine the in-plane epitaxial relationship. Six evenly spaced ZnO peaks verified that the hexagonal ZnO film was epitaxially grown on the GGO/Si(111) composite substrate. Furthermore, two sets of peaks with 3-fold symmetry were observed in the GGO {440} and {400} ϕ-scans, revealing the cube-on-cube growth of GGO on Si. These results suggest that the in-plane epitaxial relationship of this hetero-epitaxial system follows $(10\bar{1}0)_{ZnO}||\{22\bar{4}\}_{GGO}$ or $\{4\bar{2}\bar{2}\}_{GGO}||\{22\bar{4}\}_{Si}$.

TEM contrast analysis was performed to characterize the nature of the structure defects developed in the ZnO layers[5]. Bright-field cross-sectional TEM images under a two-beam contrast condition with diffraction vectors **g** equal to (0002), $(10\bar{1}0)$ and $(10\bar{1}1)$ were taken to examine the threading dislocations (TDs). We found the density of the

TDs is less than $1 \times 10^{10}\mathrm{cm}^{-2}$and the edge type TDs is the dominant component. Basal stacking faults (BSFs) were also observed in the ZnO layer, in which the intrinsic type BSF is the dominant type.[6]

Figure 2 shows the optical microscopy image of the ZnO film grown at 400°C on GGO-buffered Si. The ZnO film shows a crack-free smooth surface and exhibits outstanding optical properties as verified by LT-PL measurements at 13K (Fig. 3). The enlarged spectrum of near-band edge (NBE) region together with the peak assignment is shown in the inset. The strongest peaks at 3.358 eV is assigned to neutral donor bound exciton (D^0X). D^0X has four longitudinal optical phonon replicas located below 3.325 eV. The two-electron satellite transition is located at 3.328 eV. The PL spectrum also exhibits a negligible deep-level emission near 2.2 eV, generally recognized as defect emissions. These results demonstrated the superior optical properties of the ZnO film on Si using a GGO buffer layer.

4. Conclusions

In this work, we demonstrated the growth of high-quality and crack-free ZnO epitaxial films by PLD on Si (111) substrates with a nanometer thick GGO buffer layer. The in-plane epitaxial relationship between the wurtzite ZnO, cubic GGO and cubic Si follows $(10\bar{1}0)_{\mathrm{ZnO}}||\{22\bar{4}\}_{\mathrm{GGO}}$ or $\{4\bar{2}\bar{2}\}_{\mathrm{GGO}}||\{22\bar{4}\}_{\mathrm{Si}}$. XRD and TEM measurements reveal that the major defect structures in ZnO films are edge TDs and intrinsic BSFs. The PL results also show the excellent optical properties of the obtained ZnO layers. These results provide valuable information for the integration of ZnO-based multifunctional devices on Si substrates.

Acknowledgements

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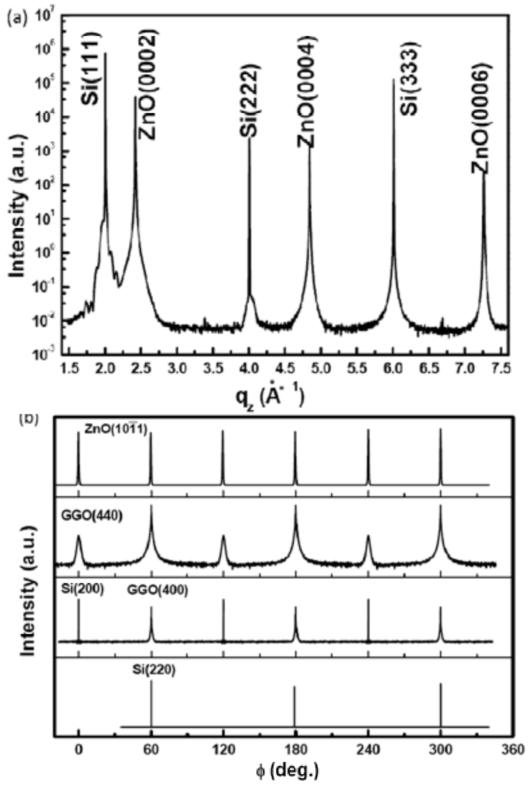

Fig. 1(a) XRD radial scan along surface normal of the ZnO film grown on GGO/Si (111); (b) ϕ-scan profiles across several off-normal reflections of ZnO, GGO and Si.

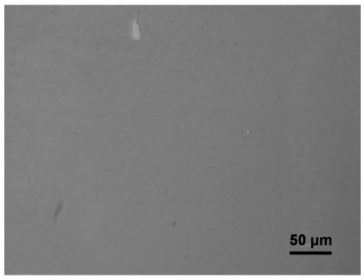

Fig. 2 Plan-view image of ZnO surface grown on a GGO-buffered Si substrate obtained using an optical microscope.

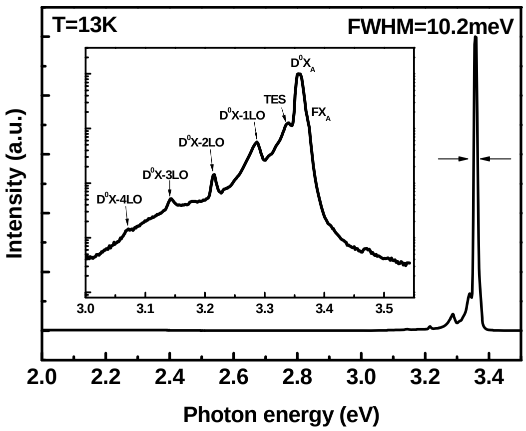

Fig. 3 PL spectra of the ZnO film on GGO/Si (111) measured at 13K. The inset is the extended spectrum of NBE emission.