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Y₂O₃ buffer layer for high-quality ZnO epitaxial growth on Si(111)W.-R. Liu,¹ Y.-H. Li,¹ W. F. Hsieh¹, C.-H. Hsu,^{1,2} W. C. Lee,³ Y. J. Lee,³ M. Hong,³ and J. Kwo⁴¹Department of Photonics & Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

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²Research Division, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan³Department of Materials Science & Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan⁴Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan**Introduction:**

ZnO based II-VI semiconductor has been viewed as a candidate for developing UV/blue light emitting diodes (LEDs) and laser diodes in next generation due to its large direct band gap of 3.37 eV and exciton binding energy of 60 meV at room temperature (RT).¹ Because of low cost, excellent quality, large-area availability of Si wafer, and unique possibility of integrating well-established Si electronics with ZnO-based optoelectronic devices, much attention has been paid on heteroepitaxially grown ZnO on Si substrate. Unfortunately, direct growth of epitaxial ZnO films on Si is an extremely difficult task due to large diversity in the mismatch of lattice constants ($\sim -15.4\%$) and thermal expansion coefficient (56%). Furthermore, due to the formation of amorphous SiO₂ layer at ZnO/Si (111) interface, it usually results in polycrystalline films with preferred orientation along growth direction.²

In this study, we report the growth of high-quality epitaxial ZnO films by pulsed-laser deposition (PLD) on a Y₂O₃/Si (111) composite substrate. The nano-thick Y₂O₃ epi-layer serves not only as a buffer layer to ensure the growth of ZnO epi-film of high structural perfection but also as an insulator layer between ZnO and Si. The structural properties of ZnO/Y₂O₃/Si(111) hetero-epitaxial system was examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Superior optical characteristics of the ZnO film were verified by photoluminescence (PL) at RT and low temperature (LT).

Experiment

The cubic Y₂O₃ buffer layer with lattice constant $a = 10.6056 \text{ \AA}$ was deposited on Si(111) substrate at 770°C, which was cleaned by RCA method, using electron beam evaporation from a high-purity Y₂O₃ source in a multi-chamber molecular beam epitaxy (MBE).³ ZnO was subsequently grown by PLD.⁴ The beam out of a KrF excimer laser ($\lambda = 248 \text{ nm}$) at a repetition rate of 10 Hz was focused to produce an energy density $\sim 5\text{--}7 \text{ J}\cdot\text{cm}^{-2}$ on a commercial hot-pressed stoichiometric ZnO (5N) target. Without introducing oxygen gas flow during growth, the ZnO layers were grown at substrate temperature ranging from 200 to 500°C. The typical ZnO layer thickness is $\sim 0.21 \text{ }\mu\text{m}$ with a growth rate $\sim 0.28 \text{ \AA}\cdot\text{s}^{-1}$ at 400°C. XRD measurements were performed with an eight-circle diffractometer at the wiggler beamline BL17B of National Synchrotron Radiation Research Center, Taiwan with incident wavelength $1.3344 \text{ \AA}$. Cross sectional TEM images were taken using a field-emission-gun type TEM (Philips

TECNAI-20). The PL measurement was carried out using a He-Cd laser with wavelength of 325 nm as pumping source and light emission was dispersed by a Triax-320 spectrometer.

Results and discussion

The radial scans (2θ - ω) XRD along the surface normal were shown in Fig. 1(a) and the ZnO (002), Y₂O₃ (222) and Si (111) reflections were observed elucidating a crystalline orientation relationship of $(002)_{\text{ZnO}} \parallel (222)_{\text{Y}_2\text{O}_3} \parallel (111)_{\text{Si}}$ for surface normal. The clear Pendellösung fringe observed near Y₂O₃ (222) reflection indicates the sharpness of the Y₂O₃ interfaces and yields a thickness of $\sim 9.6 \text{ nm}$ calculated from the fringe period. Azimuthal cone scans (Φ -scans) across the off-normal ZnO {101}, Y₂O₃ {440} and Si {220} peaks, as illustrated in Fig. 1(b), were measured to examine the in-plane epitaxial relation. Six ZnO diffracted peaks are evenly spaced 60° apart that confirms the ZnO film is epitaxially grown on Y₂O₃/Si (111) substrate. Furthermore, it is worth noticing that two sets of 3-fold symmetric peaks were observed in the Y₂O₃ {440} Φ -scan, revealing the cube-on-cube growth of Y₂O₃ on Si with two in-plane rotated variants. the dominant one, B-type (111)-orientated domain, has its in-plane orientation rotated 60° from the Si substrate; and the minor one, A-type domain, has the same angular position as that of Si {220}.³ These results suggest that the in-plane epitaxial relationship follows $\{100\}_{\text{ZnO}} \parallel \{844\}_{\text{Y}_2\text{O}_3}$ or $\{448\}_{\text{Y}_2\text{O}_3} \parallel \{224\}_{\text{Si}}$.

Typically, the lattice parameters of the ZnO layer grown at 400°C are $a = 3.2584 \text{ \AA}$ and $c = 5.1815 \text{ \AA}$ as determined by fitting the positions of Bragg reflections. As compared with its bulk values, $a = 3.2438 \text{ \AA}$ and $c = 5.2036 \text{ \AA}$ determined from a ZnO wafer, we found that the ZnO epitaxial films experience a tensile strain ($\sim 0.42\%$) in the lateral direction and a compressive strain ($\sim 0.45\%$) along the surface normal. All the other samples exhibit the same strain states with slightly different strain values. To characterize the structural quality of the grown films, the θ -rocking curve and Φ -scans of the ZnO (004) and (101) reflections were measured and shown in Figs. 1(c) and 1(d). The obtained mosaic spread of (004) is 0.27° and the full width at half maximum (FWHM) of Φ -scans of (112) reflection is 0.517° specifying high-quality crystal structure of ZnO epi-films. Especially, such a small FWHM of Φ -scans even for film with thickness of $\sim 210 \text{ nm}$ is comparable to that of ZnO film grown on (001) sapphire.⁴

The selected area electron diffraction (SAED) pattern near the interface region of the ZnO film taken along

$[11\bar{2}]_{\text{Si}}$ direction is shown in Fig. 2(a). It illustrates the in-plane crystalline orientation relationship of $\{110\}_{\text{ZnO}} \parallel \{440\}_{\text{Y}_2\text{O}_3} \parallel \{220\}_{\text{Si}}$, which is consistent with the XRD results. Figure 2(b) shows the high magnified cross-sectional TEM image at the ZnO/Y₂O₃ interface. The periodic contrast with spacing of ~ 1.31 nm, labeled by cross symbols within the dash circle, is induced by strain field. Moreover, a domain matching epitaxy (DME) of ZnO is comprehended with the 8-unit ZnO (110) cells matching the 7-unit Y₂O₃ (440) cells along $[110]_{\text{ZnO}}$ direction via periodic arrangement of misfit dislocation for resulting in -0.68% residual strain.

The RT-PL spectrum, shown in Fig. 3(a), exhibits a very weak deep-level emission (DLE) near 2.2 eV and a narrow near-band edge (NBE) emission at 3.296 eV, that is dominated by the free exciton emission. Both low DLE signals as well as the narrow and intense NBE emission are signatures of good optical performance. Figure 3(b) illustrates the LT-PL spectrum and the enlarged spectrum of the NBE region together with the peak assignment is shown in the inset. The dominant LT luminescence line at 3.358 eV with a FWHM of ~ 9.1 meV and the lines around 3.368 eV were ascribed to the recombination of A-exciton bound to the neutral donors, $\text{D}^0_2\text{X}_\text{A}$ and $\text{D}^0_1\text{X}_\text{A}$, respectively. By fitting the temperature-dependent intensity variation of the free A-exciton (FX_A) line at 3.371 eV using the Arrhenius expression, we obtained the binding energy of A-exciton 56.57 ± 6.53 meV, in good agreement with the 60 meV for bulk ZnO crystal. The other strong line at 3.329 eV ($\text{D}^0_2\text{X}_\text{A}$)_{2e} originates from the transitions involving radiative recombination of an exciton bound to a neutral donor ($\text{D}^0_2\text{X}_\text{A}$) and leaving the donor in the excited state, also known as two-electron satellite (TES). We made such assignment based on the ratio of donor binding energy to exciton binding energy ~ 0.34 as reported by Teke *et al.*⁵ The FX_A , $\text{D}^0_2\text{X}_\text{A}$ and TES emission accompanied with single phonon (FX_A -1LO, $\text{D}^0_2\text{X}_\text{A}$ -1LO and TES-1LO) replica were observed at 3.301, 3.288 and 3.26 eV, respectively, and the peak at ~ 3.22 eV is the donor-acceptor pair (DAP) transition. These results demonstrated the superior optical properties of the ZnO thin film on Si using a Y₂O₃ buffer layer.

Summary

The high-quality ZnO epitaxial films have been successfully grown by PLD on Si (111) substrates with a nano-thick Y₂O₃ buffer layer. Determined by XRD and TEM, the epitaxial relationship of the sample follows $(001)\{100\}_{\text{ZnO}} \parallel (111)\{844\}_{\text{Y}_2\text{O}_3}$ or $\{448\}_{\text{Y}_2\text{O}_3} \parallel (111)\{224\}_{\text{Si}}$. It can be described by domain matching epitaxy with 8-unit of ZnO (110) cells matching 7-unit of Y₂O₃ (440) cells which leads to significantly reducing residual strain. Superior optical properties were obtained even for ZnO-films as thin as 210 nm from room-temperature photoluminescence.

Acknowledgments

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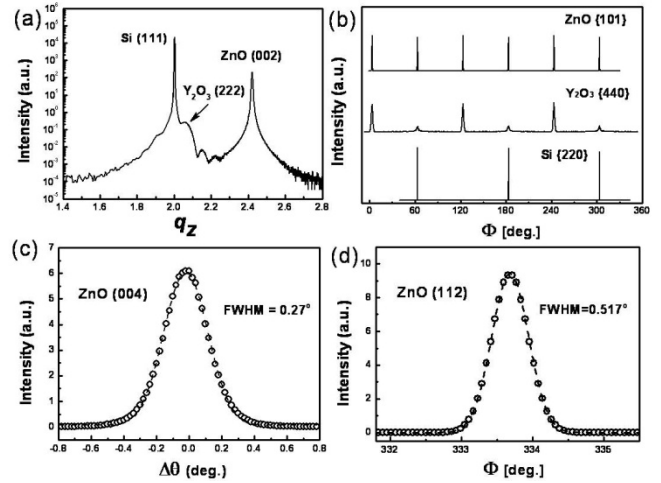


Fig. 1. XRD spectra of the ZnO film on Y₂O₃/Si (111). (a) radical scan along surface normal; (b) Φ -scan profiles of ZnO/Y₂O₃/Si(111) structure: ZnO{101}, {404} and {400} of Y₂O₃, and Si {220} planes; (c) θ -rocking curve of ZnO (004) plane; and (d) Φ -rocking curve of ZnO (112) plane.

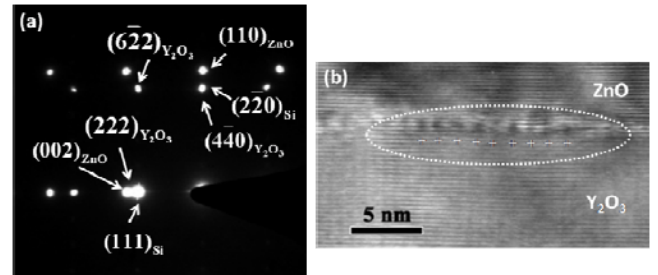


Fig. 2 The SAED pattern along $[11\bar{2}]_{\text{Si}}$ direction near the interface region (a); the HR-TEM image with periodic contrast at ZnO/Y₂O₃ interface, as marked by cross symbols within a dash circle (b).

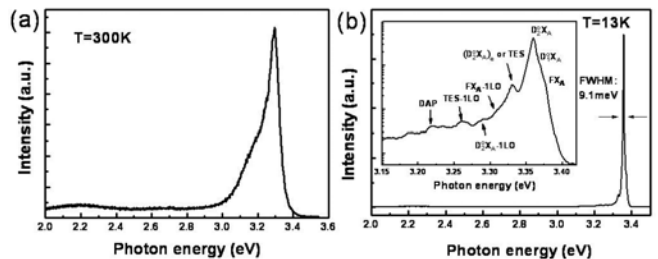


Fig. 3. PL spectra of the ZnO film on Y₂O₃/Si (111) measured at 300 K (a) and 13 K (b). The inset in (b) is the extended spectrum of near-band edge emission.