

# Crystal growth and optical characterizations of nonpolar $m$ -plane ZnO on the $m$ -plane sapphire substrate by PLD

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## 1. Introduction

The wide-band-gap semiconductor ZnO with a wurtzite structure is popular for application in ultraviolet (UV) light emitting devices (LEDs) and laser diodes (LDs). ZnO is a potential candidate for optoelectronic applications due to and the larger exciton binding energy (60 meV) over GaN (25 meV). Usually, ZnO epilayers often grow preferentially with  $c$ -plane normal which consists of alternative layers of Zn cations and O anions along the growth direction. There is a net dipole field along the  $c$ -axis from the crystallographic structure. However, considering LEDs or LDs with the ZnO-based devices, we will encounter the problem of the quantum-confined Stark effect (QCSE) due to piezoelectric and spontaneous polarizations in the  $c$ -axis oriented ZnO structure. Non-polar surfaces such as  $a$ -plane ( $1\bar{1}20$ ) and  $m$ -plane

( $10\bar{1}0$ ) have been proposed to avoid built-in electric fields to improve quantum efficiency.

Recent reports have shown the strong strain effect in the  $a$ -plane ( $1\bar{1}20$ ) ZnO thin film [1, 2]. The nonpolar  $a$ -ZnO films on  $r$ -sapphire have significant residual anisotropic strains induced by lattice and thermal expansion mismatches. The XRD results revealed the in-plane anisotropic strain causes crystal symmetry breaking from wurtzite ( $C_{6v}$ ) to orthorhombic ( $C_{2v}$ ). This structure transformation accounts for the observed different optical transition in polarized optical reflection and photoluminescence (PL) spectra confirm the anisotropic strain causes the structure change to the orthorhombic one. [2, 3] These effects are a disadvantage when we design the quantum wells LEDs and LDs. The  $m$ -plane ZnO structure should be a good choice to grow nonpolar ZnO structure.

## 2. Methods of fabrication

Nonpolar  $m$ -plane ZnO film of thickness about 500 nm was grown on  $Al_2O_3(30\bar{3}0)$  using pulsed laser deposition using KrF (248 nm) laser. The ZnO source was from 5N ZnO target. During the deposition, the substrate temperature was maintained at 450 to 600 °C. The x-ray diffraction (XRD) measurements were performed with a four-circle diffractometer at beamline BL13A of National Synchrotron Radiation Research Center, Taiwan with incident wavelength of 1.0305 Å. Low temperature photoluminescence (LT-PL) spectra were performed at 13

K in use of a He–Cd laser at 325 nm as the pump source. Through a UV polarizer with pass band ranging from 280 to 400 nm, the PL was analyzed by a Triax-320 spectrometer equipped with a UV-sensitive photomultiplier tube.

## 3. Results and discussion

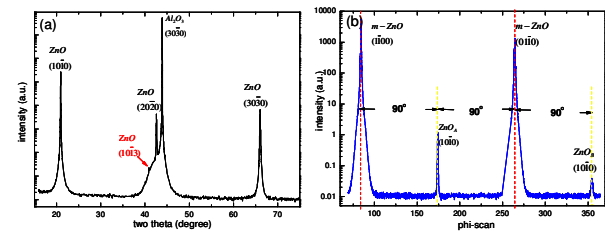


Fig. 1 The XRD patterns with (a) the radial scan along surface normal, in which ZnO ( $10\bar{1}0$ ) and sapphire ( $10\bar{1}0$ ) reflections dominate, weak  $ZnO(10\bar{1}3)$  domain marked by arrow was also observed; and (b) the off-normal reflection shows azimuthally phi-scans across the ZnO  $\{1\bar{1}00\}$  and two ( $10\bar{1}0$ ) planes resulting from the  $m$ -ZnO and two other  $ZnO(10\bar{1}3)$  domains.

The XRD patterns of the radial scan along the surface normal and the phi scan are illustrated in Figure 1. Fig. 1(a) shows apparent diffraction peaks of the  $ZnO\{10\bar{1}0\}$  and  $Al_2O_3(30\bar{3}0)$  confirming the  $m$ -plane ZnO epi-layer growth. The off-normal scan has two reflection peaks at ( $01\bar{1}0$ ) and ( $1\bar{1}00$ ) separated by 180° apart revealing the in-plane orientation of  $m$ -ZnO. In addition, there is an extra peak near the  $ZnO(20\bar{2}0)$  peak in the surface scan being identified as  $ZnO(10\bar{1}3)$  and two ( $10\bar{1}0$ ) peaks belong to two separate  $ZnO(10\bar{1}3)$  domains. We therefore yields the in-plane epitaxial relationship of  $ZnO[0002] \parallel ZnO_{A,B}[10\bar{1}\bar{1}] \parallel Al_2O_3[1\bar{1}20]$ .

The calculated lattice constants of both the  $a$ - and  $c$ -axes from the XRD data show very small strains that differ from the previous report. [4] The existence of A and B domains  $ZnO_{A,B}(10\bar{1}3)$  provides space for strain relaxation of the  $m$ -ZnO so that it behaves as a free-strain layer. In addition, by comparing the peak intensity ratio of the XRD from the ( $10\bar{1}3$ ) and the ( $10\bar{1}0$ ) domains with that of the JCPD card 36-1451 (0.5089), representing equal weight of

(10 $\bar{1}$ 3) and (10 $\bar{1}$ 0) planes, we deduced the contain of the (10 $\bar{1}$ 3) domains within the regular m-ZnO to be less than  $2.22 \times 10^{-3}$ . The small ratio represents for the dominant m-ZnO growth on the *m*-sapphire. The peak ratio also depends on the growth temperature, the smallest ratio occurs for the growth temperature of 500°C, so this sample possesses the least (10 $\bar{1}$ 3) domains. These results are confirmed with HRTEM images, in which one could barely see extra (10 $\bar{1}$ 3) domains.

The normalized LT-PL spectra show a sharp near-band edge (NBE) around 3.36 eV and a weak broad band around 3.16 eV due to the deep-level emission in Fig. 2 (a). The stronger broad-band emission is correlated with the higher (10 $\bar{1}$ 3) domains. It may result from the more (10 $\bar{1}$ 3) domains the more domain boundary existing between the regular m-ZnO and the (10 $\bar{1}$ 3) domains. Moreover, the larger surface-to-volume ratio for the more (10 $\bar{1}$ 3) domains makes the surface-bound exciton emission increased. Reparaz *et al.* have reported the surface bound exciton (SX) emission shifts to the lower energies with increasing emission intensity as decreasing the wire diameter. The surface-bound states and defects in the grain boundary contribute to the SX emission at around 3.17 eV. Therefore, the lowest SX emission indicates the least (10 $\bar{1}$ 3) domains in the 500°C-grown sample.

The polarized LT-PL shown in Fig. 2(b) exhibit exciton peaks located at 3.379, 3.388 and 3.443 eV are attributed to free A-, B- and C-excitons (FXA, FXB and FXC), respectively. The other NBE emission around 3.36 eV is attributed to the neutral donor-bound exciton peak and the two-electron satellite (TES) of donor-bound exciton is located at 3.32 eV. We can see that the broad-band SX emission near 3.17 eV is sensitive to the polarization.

It is known that the FXA and FXB are excited when the (excitation) polarization is perpendicular to the c-axis (E $\perp$ c), whereas, the FXC is active when the polarization is parallel to the c-axis (E//c). Because the absorption cross-sections of the FXA and FXB are much larger than that of FXC, we can see in Fig. 2(b) the relatively small FXC accompanied with a stronger (10 times intensity of FXC) SX emission for E//c. However, for E $\perp$ c we observed about 40 times intense FXA with comparable SX emission. These results should depend upon the efficiency of exciting excitons followed by bound to the surface states at the boundary between (10 $\bar{1}$ 0) and (10 $\bar{1}$ 3) domains. Due to the relative low contain of the (10 $\bar{1}$ 3) domains, for E//c PL spectrum the FXC mostly originate from the excitation of m-ZnO rather than the (10 $\bar{1}$ 3) domains. Furthermore, we can see that the FXA/FXB on the high-energy shoulder of DX may be attributed to emission from the (10 $\bar{1}$ 3) domains that were excited by the component of E $\perp$ c and the bound FXA/FXB contribute to DX and SX emission, being > 10 times larger than the FXC. On the other hand, for E $\perp$ c excitation, both m-ZnO and

(10 $\bar{1}$ 3) domains are efficiently excited to form FXA/FXB, in turn the larger surface-to-volume value of the (10 $\bar{1}$ 3) domains contribute most of the SX emission as a result of the FX being captured by the surface defects. Therefore, the comparable SX and FXA/FXB emission result. In addition, by subtracting the circularly or non-polarized excited PL to the E $\perp$ c one, we approximately obtain the intensity of SX with the E//c excitation.

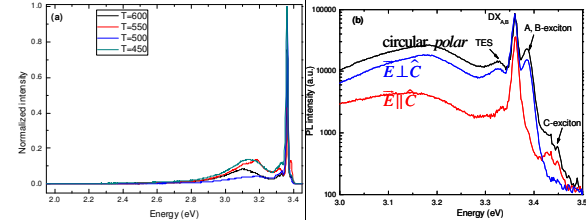


Fig. 2 (a) The PL spectra of the m-ZnO grown on different temperature m-sapphire substrates at 13K were shown strong NBE and broad band emission without deep level transitions. (b) Polarized PL spectra of the *m*-ZnO epilayer grown at 450 °C taken in various polarization configurations at 13 K.

#### 4. Conclusions

We have successfully grown nonpolar (100) ZnO thin film on the m-Al<sub>2</sub>O<sub>3</sub> substrate by PLD. The XRD showed the strong (10 $\bar{1}$ 0) domain existed with slightly strained and the weak (10 $\bar{1}$ 3) peak is free-strained. LT-PL spectra showed the free A-, B- and C-exciton peaks close to the bulk ZnO due to the slight strain. The broad band peak should be surface bound exciton at the boundary between m-ZnO and (10 $\bar{1}$ 3) domains and the SX emission is correlated to the intensity ratio of (10 $\bar{1}$ 3)/(10 $\bar{1}$ 0).

#### Acknowledgements

This work is partially supported by National Science Council of Taiwan under Grants NSC-99-2112-M-006-017-MY3 and NSC 100-2112-M-006-002-MY3.

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