TuAA2
16.00 - 16.15

# Crystal symmetry breaking of wurtzite to orthorhombic in nonpolar *a*-ZnO epi-films

C. C. Kuo,[a)] W. -R. Liu,[a,c)] and W. F. Hsieh,[*a,b)] C.-H. Hsu,[*c,a)] H. C. Hsu,[d)] and L. C. Chen[d)]
[a)] Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan.
[b)] Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan 70101 Taiwan.
[c)] Scientific Research Division, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.
[d)] Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.

***Abstract-*** **Crystal symmetry breaking of wurtzite $C_{6V}$ to orthorhombic $C_{2V}$ due to in-plane anisotropic strain was investigated for nonpolar a-ZnO epi-films grown on R-sapphire.**

## I. INTRODUCTION

Wurtzite ZnO (a = 3.2438 Å and c = 5.2036 Å) is a wide bandgap semiconductor with $E_g$ = 3.37 eV at room temperature. The driving force for its photonic applications is the stability of ZnO free exiton having a large binding energy of 60 meV. It has potential uses in transparent conductive films, UV LEDs and photodetectors. The non-centrosymmetric crystallographic structure consisting of alternative layers of Zn cations and O anions along the *c*-axis leads to a net dipole field. Due to this polar feature, the piezo- and pyroelectric effects cause the so-called quantum confined Stark effect to degrade not only the band gap but also the optical properties of *c*-plane multiple quantum wells. Orienting the *c*-axis of ZnO on the substrate plane is a solution to this problem and renders a new trend of using nonpolar oriented epi-layers for the applications to the efficient photonic devices [1-2]. Ref. [1] reported that the anisotropic strains changed the crystal symmetry of ZnO and hence the A, B, and C excitonic transitions of wurtzite ZnO with $C_{6V}^4$ space group could no longer be used. The biaxial strain breaks the $C_{6V}$ crystal symmetry and changes its optical transitions [3-4]. The nomenclature $E_1$, $E_2$, and $E_3$ were adapted for the ground state of the three excitons to describe exciton structures of the deformed GaN [3]. This phenomenon should also happen in nonpolar ZnO systems but are rarely reported.

## Ⅱ. EXPERIMENTAL

Nonpolar *a*-plane, $(11\bar{2}0)$, ZnO film of thickness about 1.2 μm was grown on *r*-plane, $(01\bar{1}2)$, sapphires using pulsed laser deposition. During the deposition, the chamber pressure ~ $2\times10^{-8}$ torr and substrate temperature at 400 ~ 600°C were maintained. The X-ray diffraction (XRD) measurements were performed with a four-circle diffractometer at beamline BL13A of National Synchrotron Radiation Research Center (NSRRC), Taiwan with incident wavelength of 1.0305 Å. The polarized mirco-Raman spectra with excitation wavelength of He–Ne laser (632.8 nm) was recorded by a LabRam HR800 (Jobin–Yvon, France) spectrometer. A He-Cd laser radiating at 325 nm was used as the pumping source for photoluminescence (PL) and a broad-band light source (Spex 1682A) was utilized for optical reflection (OR) measurements at 13K. Through an UV polarizer with pass band ranging from 280 to 400 nm, the PL and the reflected light was collected by a Triax-320 spectrometer equipped with an UV-sensitive photomultiplier tube.

## Ⅲ. RESULTS AND DISSCUSION

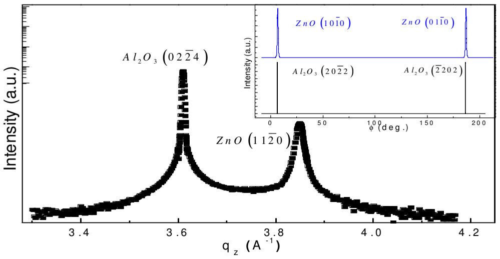

Fig. 1. XRD radial scan along surface normal, in which only the ZnO $(11\bar{2}0)$ and sapphire $(02\bar{2}4)$ reflections were observed. The inset shows azimuthally $\phi$-scans across the ZnO $\{10\bar{1}0\}$ and sapphire $\{20\bar{2}2\}$ off-normal reflections.

Figure 1 illustrates an XRD radial scan along the surface normal. In addition to the $(02\bar{2}4)$ reflection from the *R*-sapphire substrate, only ZnO $(11\bar{2}0)$ reflection and its harmonic were observed that confirms the *a*-plane orientation of the ZnO layer. We also performed azimuthal $\phi$-scans across ZnO $\{10\bar{1}0\}$ and sapphire $\{20\bar{2}2\}$ off-normal reflections (see inset of Fig. 1) to examine relative in-plane orientation. The two peaks, which are 180° apart, are $(10\bar{1}0)$ and $(01\bar{1}0)$ reflections of ZnO and $(20\bar{2}2)$ and $(\bar{2}202)$ peaks of sapphire, respectively. The coincidence of the angular positions of ZnO $(10\bar{1}0)$ and sapphire $(20\bar{2}2)$ yields the in-plane epitaxial relationship of $[0001]_{ZnO} \parallel [0\bar{1}11]_{sapphire}$. Deriving from peak positions, we determined the inter-planar spacing, *d*, associated with three mutually orthogonal planes, $(11\bar{2}0)$, $(1\bar{1}00)$, and (0002), of the ZnO epi-layer are 1.6374, 2.8185, and 2.582 Å, respectively. The ratio $d_{(1\bar{1}00)}/d_{(11\bar{2}0)}$ = 1.721 deviated from the expected value for a hexagonal lattice, $\sqrt{3}$, signifies the breaking of hexagonal symmetry and the transformation of the lattice into an orthorhombic one.

978-1-4244-3681-1/09/$25.00 ©2009 IEEE

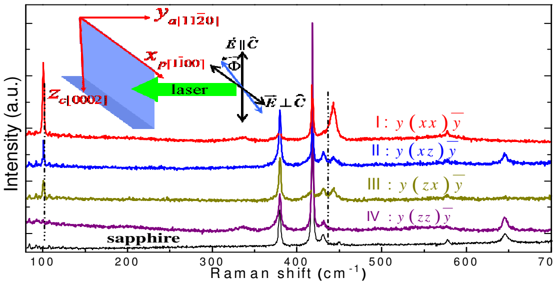

Fig. 2 Polarized Raman spectra taken in 4 distinct backscattering configurations. A spectrum of bare sapphire substrate is also plotted for comparison. The dashed lines at 101 and 436 cm$^{-1}$ mark respectively the positions of $E_2^{(low)}$ and $E_2^{(high)}$ modes of bulk ZnO. A schematic of the scattering geometry is also shown in the inset.

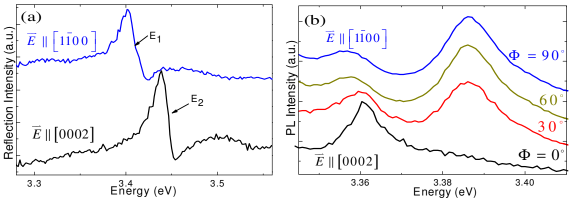

Fig. 3. (a) polarized optical reflection and (b) polarized PL spectra of the *A*-ZnO epi-layer taken in various polarization configurations at 13K.

Raman scattering is governed by the polarization dependent selection rules imposed by the crystal symmetry and is sensitive to strain state. The polarized Raman spectra taken under the four distinct backscattering geometries, Ⅰ, Ⅱ, Ⅲ and Ⅳ, are shown in Fig. 2. The peaks at 378.3, 417.0, 429.4, 576.1, and 644.1 cm$^{-1}$ originate from sapphire. Examining the two Raman peaks at ~100.6 and ~443.0 cm$^{-1}$, we observed red shift for $E_2^{(low)}$ mode but blue shift for $E_2^{(high)}$ mode with respect to the bulk values. It implies a compressive strain within the basal plane and a tensile strain along the *c*-axis, provided that the wurtzite crystal structure is assumed. However, this is inconsistent with our XRD observations, i.e., biaxial tensile strain within the *x*-*y* plane and compressive strain along the *c*-axis. This contradiction can be resolved by changing the crystal structure from hexagonal to orthorhombic symmetry because anisotropic biaxial strains within the basal plane can further lift the symmetry in this nonpolar plane of the wurtzite structure [3-4].

For a crystal with the $C_{2V}$ symmetry, there are 24 Raman active modes with the corresponding Raman matrix elements $A_{1g} = (\alpha_{xx}, \alpha_{yy}, \alpha_{zz})$, $B_{1g} = (\alpha_{xy}, \alpha_{yx})$, $B_{2g} = (\alpha_{xz}, \alpha_{zx})$, and $B_{3g} = (\alpha_{yz}, \alpha_{zy})$ [5]. Under the current experimental geometry with laser traveled along the *y* axis, the $B_{1g}$ and $B_{3g}$ modes were not accessible. The peaks at 100.7 and 443.6 cm$^{-1}$ appeared in both Ⅱ and Ⅲ configurations and hence were of $B_{2g}$ symmetries. Two nearby peaks at 100.5 and 442.7 cm$^{-1}$ were observed in configuration-I suggesting they are $A_{1g}$ modes. Although the peak positions of $A_{1g}$ and $B_{2g}$ modes are very close, we distinguished those modes by the polarized selection rules and their intensities because the $B_{2g}$ modes are expected to be significantly weaker than the $A_{1g}$ modes [5]. So, in configuration-I, these two Raman peaks are attributed to the $A_{1g}$ mode; in Ⅱ and Ⅲ configurations, they are attributed to the $B_{2g}$ modes. Based on the $A_{1g}$ Raman tensor, 100.5 and 442.7 cm$^{-1}$ peaks should also appear in configuration-IV but we didn't observe them. This phenomenon was also reported by Ref. [5] on an orthorhombic structure. Besides, the broad peak at ~340 cm$^{-1}$ appears in Ⅰ and Ⅳ that also attributed to the $A_{1g}$ mode from the Raman tensor. The observed polarization dependence of the Raman spectra of the a-ZnO epi-layer is consistent with the breaking of $C_{6V}$ symmetry and the polarization selection rules of orthorhombic structure with $C_{2V}$ symmetry.

Due to the wurtzite symmetry breaking, we would expect different optical properties of biaxially strained *a*-ZnO films from that of ZnO bulk. To further examine the influence of crystal structure change on the optical properties of ZnO films, we performed OR at 13 K as presented in Fig. 3(a). Two transitions at 3.412 and 3.449 eV were observed respectively in $E \perp c$ and $E \parallel c$ configurations and their energies are larger than those of *A*, *B*, and *C* excitons of bulk ZnO [1, 3]. We assigned the former to $E_1$ and the latter to $E_2$ transitions [1, 3], which were also observed in PL spectra. Figure 3(b) shows the polarized PL spectra taken with the polarization angle Φ at 0°, 30°, 60°, and 90° with respect to the crystalline *c*-axis. The increasing intensity ratio of the main PL peaks at 3.386 and 3.358 eV as increasing Φ is also complied with the polarization selection rules for $E_1$ and $E_2$ transitions [1].

## Ⅳ. CONCLUCTION

In conclusion, the nonpolar *a*-plane ZnO films on *R*-plane 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 to orthorhombic for the nonpolar a-ZnO epi-layer. The polarization dependence of polarized Raman, OR and PL spectra all agree with the polarization selection rules associated with C$_{2V}$ symmetry.

## ACKNOWLEDGMENT

This work is partly supported by National Science Council of Taiwan under grants NSC-96-2628-M-009-001-MY3 and NSC-96-2119-M-213-003.

## REFERENCES

[1] T. Koida, S. F. Chichibu, A. Uedono, T. Sota, A. Tsukazaki and M. Kawasaki, Appl. Phys. Lett. **84**, 1079 (2004).
[2] Y. S. Nam, S. W. Lee, K. S. Baek, S. K. Chang, J. H. Song, J. H. Song, S. K. Han, S. K. Hong, and Takafumi, Appl. Phys. Lett. **92**, 201907 (2008).
[3] S. Ghosh, P. Waltereit, O. Brandt, H. T. Grahn, and K. H. Ploog, Phys. Rev. B **65**, 075202 (2002).
[4] B. Gil and A. Alemu, Phys. Rev. B **56**, 12446 (1997).
[5] M. N. Iliev, M. V. Abrashev, H.-G. Lee, V. N. Popov, Y. Y. Sun, C. Thomsen, R. L. Meng, and C. W. Chu, Phys. Rev. B **57**, 2872 (1998).