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Growth of nonpolar (11$\bar{2}$0) ZnO films on $LaAlO_3$ (001) substrates

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Nonpolar (11$\bar{2}$0) ZnO films were grown on $LaAlO_3$ (001) single crystal substrates at temperature from 300 to 750 °C by pulsed laser deposition method. The films were examined using x-ray diffraction, reflection high energy electron diffraction, and photoluminescence measurements for the crystallinity. The surface morphology of ZnO films from atomic force microscopy exhibits L-shaped domains. Cross-sectional transmission electron microscopy with selected area diffraction reveals two types of *a*-plane ZnO domains perpendicular to each other with in-plane orientation relationships of $[0001]_{ZnO} \| [1\bar{1}0]_{LAO}$ and $[1\bar{1}00]_{ZnO} \| [1\bar{1}0]_{LAO}$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2988167]

As a promising material for the application in ultraviolet optoelectronic devices, ZnO thin films have attracted much attention due to their wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature. As for group III nitrides, there exists an electrostatic field within the active layer along the *c*-axis of hexagonal ZnO. The quantum confined Stark effect (i.e., polarization effect) will greatly affect the luminous efficiency of light emitting diodes and laser diodes. Consequently, it is preferable to grow high-quality nonpolar ZnO in *a*-plane and *m*-plane. Deposition of nonpolar ZnO epitaxial films has been reported on *r*-plane sapphire, $SrTiO_3$, (La,Sr)(Al,Ta)O_3, etc.[1–3] Among them, *r*-plane sapphire is the most commonly used substrate for *a*-plane ZnO film deposition.[4,5] Despite the advantages in thermal stability and its low cost, *r*-plane sapphire inherits a great disadvantage of large anisotropic lattice mismatch (~18.2%) with ZnO along [1$\bar{1}$00],[4] which will greatly reduce the *a*-plane ZnO crystalline quality by generating a high density of dislocations.

To improve the crystalline quality, it is highly desirable to choose a suitable substrate that exhibits a smaller lattice mismatch with ZnO. Accordingly, we adopted $LaAlO_3$ as a substrate to study the growth of ZnO due to its pseudocubic structure with lattice constant of 3.793 Å (Ref. 6) and the small lattice mismatches between ZnO and $LaAlO_3$ of 3% and 5% for $\langle 110 \rangle_{LAO}$ (45 degree rotation of $\langle 100 \rangle_{LAO}$) along the directions of ZnO[0001] and [10$\bar{1}$0], respectively.

Lee *et al.*[7,8] demonstrated in their studies of the growth of GaN on $LaAlO_3$ (100) using molecular beam epitaxy that only *c*-plane GaN films were formed. However, previous report of growth of *a*-plane ZnO films on $LaAlO_3$ (100) substrates is rarely found. In this letter, we demonstrated that pure (11$\bar{2}$0) ZnO films (*a*-plane ZnO) could be grown on $LaAlO_3$ (100) single crystal substrates in a wide range of deposition temperatures.

The growth of ZnO films was performed in a DCA PLD500 pulsed laser deposition (PLD) system with a pulsed KrF-excimer laser of 248 nm wavelength. A 2 in. ceramic ZnO target (99.99% purity) was used for ablation. After being cleaned in boiling acetone and isopropyl alcohol, a $LaAlO_3$ (100) substrate 2 in. diameter was loaded into the PLD chamber. The substrate temperature (T_s) for ZnO deposition was varied in the range of 150–750 °C. For ZnO deposition, the oxygen partial pressure was kept around 20 mTorr, and a laser energy density of 1–2 J/cm^2 with 3 Hz repetition frequency was used. To monitor the surface morphology during growth, reflection high energy electron diffraction (RHEED) patterns were taken from an Oxford Scientific OS-RHEED system operated at 15 kV. The crystallinity of ZnO thin films was examined using a Bruker D8 x-ray diffractometer for $\theta/2\theta$ scan and a Bede D1 one for ω scan. Transmission electron microscopy (TEM) for microstructural observations in cross section was performed in a FEI Tecnai 20 microscope. Photoluminescence (PL) measurements at room temperature were carried out using a He–Cd laser (325 nm, 35 mW) as the excitation source.

All ZnO films deposited on $LaAlO_3$ by PLD have been proved to be optically transparent. Figure 1 shows typical θ–2θ x-ray diffraction (XRD) patterns of the ZnO films deposited at different substrate temperatures. We observed only the reflection of (11$\bar{2}$0) ZnO without any detectable peak

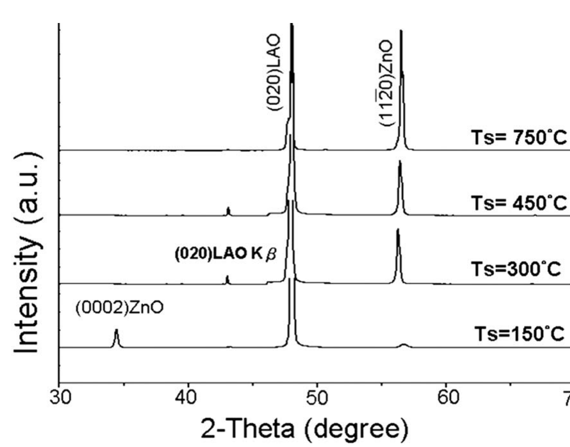

FIG. 1. XRD patterns of ZnO films grown on $LaAlO_3$ (001) substrates at different growth temperatures.

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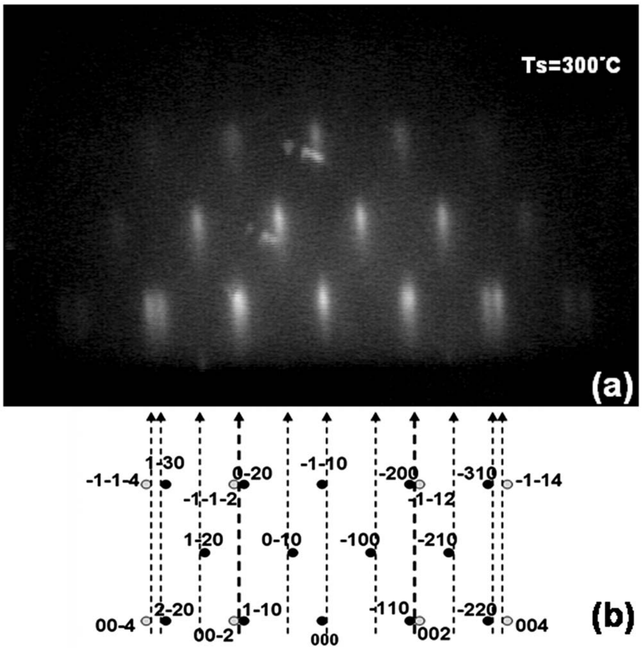

FIG. 2. (a) RHEED pattern of *a*-plane ZnO grown on LAO at 300 °C taken from *e*-beam incidence along $\langle 110 \rangle_{LAO}$ azimuth. (b) Schematic drawing of $[0001]_{ZnO}$ (white color) and $[01\bar{1}0]_{ZnO}$ (blue color) zone-axis patterns. The dash lines are corresponding to the positions of reflections in the RHEED pattern.

from (0002) ZnO for T_s=300–750 °C. This demonstrates that pure *a*-plane ZnO films can be achieved on $LaAlO_3$ (100). However, the strong (0002) peak in addition to $(11\bar{2}0)$ was detected for T_s=150 °C. In the literature, it has been shown that the temperature plays a strong role in surface termination of $LaAlO_3$ (100). The surface is La–O (LaO) plane at temperature above 250 °C, while it is only Al–O (AlO_2) plane below 150 °C.[9] Examination of the bonding in the Al–O and La–O terminated planes on $LaAlO_3$ (100) reveals that the O–O bonding distance is 2.68 and 5.36 Å, respectively. If the O sites of substrate surface provide a template for bonding with Zn of ZnO, the La–O plane may provide better match (3%–5% lattice mismatch) for growth of *a*-plane ZnO at temperature above 250 °C. In contrast, the large lattice mismatch of ZnO with the Al–O surface of $LaAlO_3$ at the substrate temperature of 150 °C may result in formation of *c*-plane and *a*-plane ZnO. The x-ray rocking curve (XRC) analysis of $(11\bar{2}0)$ in ω scan shows that the full width at half maximum (FWHM) is about 0.45°, suggesting that the crystalline quality of *a*-plane ZnO is comparable to ZnO films deposited on *r*-plane sapphire.[10] Also, there is no much difference in XRC FWHM data at different x-ray azimuths. For the ZnO grown on *r*-sapphire, it is often observed that there is a difference in XRC FWHM data measured with x-ray beam along the direction parallel and orthogonal to the in-plan *c*-axis of ZnO.[11] It is mainly due to the cubic symmetry and smaller lattice mismatch between ZnO and $LaAlO_3$ along $[10\bar{1}0]_{ZnO}$, as shown below.

Figure 2(a) shows a typical RHEED pattern of ZnO grown on LAO substrate at 300 °C by the electron beam incident azimuth along $[110]_{LAO}$. The RHEED pattern exhibits streaky features, suggesting that the film deposition is in three-dimensional growth mode with a relatively smooth surface. The same characteristics were observed on RHEED

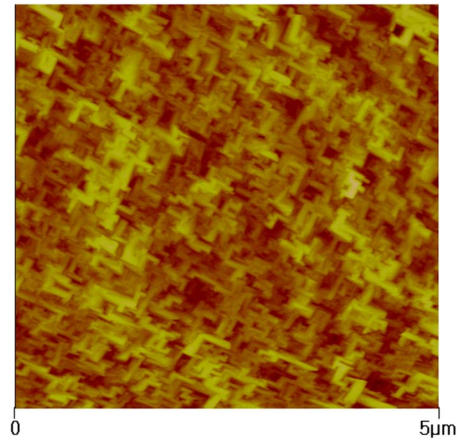

FIG. 3. (Color online) AFM image of *a*-plane ZnO film grown on LAO substrate at 750 °C.

patterns of ZnO deposited at T_S of 450, 600, and 750 °C. Rotation of 90° of azimuth angle for taking the RHEED patterns gave the same pattern such that fourfold symmetry could be identified. To explain the findings above, we suggest that there exist two kinds of growth domains perpendicular to each other in $(11\bar{2}0)$ ZnO grown on LAO. The schematic diagram in Fig. 2(b) shows that the reflections in the RHEED are indexed as in $[0001]_{ZnO}$ and $[01\bar{1}0]_{ZnO}$ zone-axis patterns.

A typical atomic force microscopy (AFM) image of an *a*-plane ZnO film (T_s=750 °C) is shown in Fig. 3, exhibiting an L-shaped morphology with the average length of 200 nm. Each L-shaped region consists of a ZnO domain, which is arranged as chevronlike relationship with adjacent L-shaped domains as evidenced by plan-view TEM (not shown). The root-mean-square surface roughness of the ZnO film is about 3.5 nm. The development of the L-shape domains is not clearly understood at present.

A bright field cross-sectional TEM micrograph with a corresponding selected-area diffraction (SAD) pattern from a sample grown at T_s=750 °C is shown in Fig. 4. The electron beam direction is approximately along ⟨110⟩ LAO. The grain contrast can be seen in the micrograph, and the ZnO/LAO interface is quite abrupt without any interlayer. The SAD pattern in Fig. 4(b) reveals that the *c*-axis and *m*-axis ZnO domains coexist together as evidenced in the RHEED and AFM results. Furthermore, a high-resolution TEM image in Fig. 4(c) taken around the ZnO/LAO interfacial region shows two adjacent ZnO grains or domains on LAO with an atomically sharp interface. Also, the domain boundary between these two domains remains coherent. The fast Fourier transform (FFT) patterns from each region are shown in the insets of Fig. 4(c), confirming that the *a*-plane ZnO grains are aligned with [0001] and $[10\bar{1}0]$ along the horizontal direction. Consequently, the orientation relationships between ZnO and $LaAlO_3$ can be deduced as $(11\bar{2}0)_{ZnO} \| (100)_{LAO}$, $[0001]_{ZnO} \| [110]_{LAO}$, and $[10\bar{1}0]_{ZnO} \| [110]_{LAO}$.

For characterization of optical properties, emissions from the ZnO sample grown on $LaAlO_3$ at 750 °C were measured using PL technique at room temperature. The spectrum in Fig. 5 shows a strong band-edge emission peak at 3.30 eV of the FWHM value of 112 meV with negligible green emission, implying that the quality of the deposited

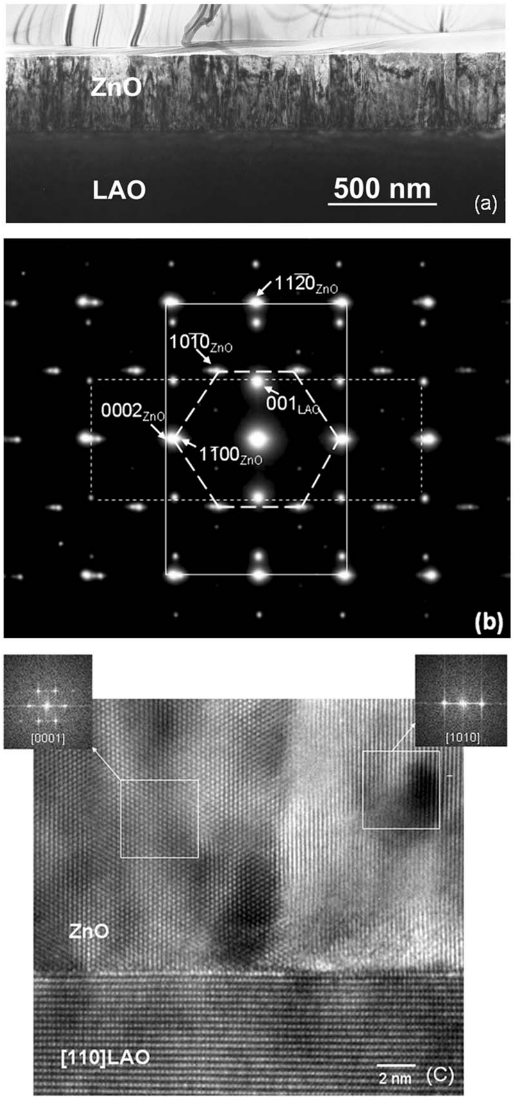

FIG. 4. (a) Bright field cross-sectional TEM micrograph of ZnO film grown on LAO substrate at 750 °C, (b) the corresponding SAD pattern, and (c) high-resolution TEM micrograph. The insets in (c) show FFT patterns of framed areas.

a-plane ZnO is similar to the result of epitaxial *a*-plane ZnO on *r*-plane sapphire.[12] Although there are two types of orthogonal domains in the formation of *a*-plane ZnO films on $LaAlO_3$ that increase the area of domain boundaries, interestingly, they do not enhance the defect density of deep level states.

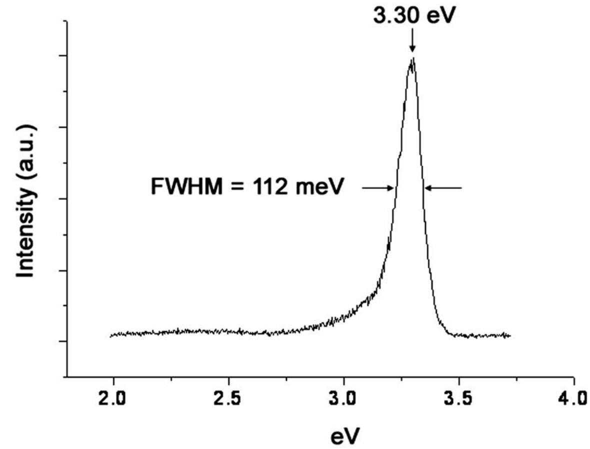

FIG. 5. Room-temperature PL spectrum of ZnO grown on LAO at 750 °C.

In summary, we have demonstrated that pure *a*-plane ZnO films can be grown on (100) $LaAlO_3$ substrates at growth temperature above 300 °C. In the *a*-plane ZnO thin films, two types of ZnO domains are formed with coherency and arranged in L-shape with their *c*-axes perpendicular to each other. The interface between ZnO and LAO is atomically sharp without formation of any interlayer.

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[1]A. Ohtomo and A. Tsukazaki, Semicond. Sci. Technol. **20**, S1 (2005).
[2]E. Bellingeri, D. Marr'e, I. Pallecchi, L. Pellegrino, G. Canu, and A. S. Siri, Thin Solid Films **486**, 186 (2005).
[3]T. Nakamura, H. Minoura, and H. Muto, Thin Solid Films **405**, 109 (2002).
[4]S. S. Kim, J. H. Je, and J. H. Kim, Phys. Status Solidi C **1**, 2541 (2004).
[5]T. Moriyama and S. Fujita, Phys. Status Solidi C **3**, 726 (2006).
[6]H. Kawanowa, H. Ozawa, M. Ohtsuki, Y. Gotoh, and R. Souda, Surf. Sci. **506**, 87 (2002).
[7]J. J. Lee, K. Y. Kang, Y. S. Park, C. S. Yang, H. S. Kim, K. H. Kim, T. W. Kang, S. H. Park, and J. Y. Lee, Jpn. J. Appl. Phys., Part 1 **38**, 6487 (1999).
[8]J. J. Lee, Y. S. Park, C. S. Yang, H. S. Kim, K. H. Kim, K. Y. Kang, T. W. Kang, S. H. Park, and J. Y. Lee, J. Cryst. Growth **213**, 33 (2000).
[9]J. Yao, P. B. Merrill, S. S. Perry, D. Marton, and J. W. Rabalais, J. Chem. Phys. **108**, 1645 (1998).
[10]S. K. Han, S. K. Hong, J. W. Lee, J. Y. Lee, J. H. Song, Y. S. Nam, S. K. Chang, T. Minegishi, and T. Yao, J. Cryst. Growth **309**, 121 (2007).
[11]J. M. Chauveau, C. Morhain, B. Lo, B. Vinter, P. Vennegues, M. Laugt, D. Buell, M. Tesseire-Doninelli, and G. Neu, Appl. Phys. A: Mater. Sci. Process. **88**, 65 (2007).
[12]C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lu, M. Wraback, and H. Shen, J. Appl. Phys. **85**, 2595 (1999).