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Growth and characterization of polar and nonpolar ZnO film grown on sapphire substrates by using atomic layer deposition

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ABSTRACT

We investigated the electrical and the optical properties of polar and nonpolar ZnO films grown on sapphire substrates with different crystallographic planes. High resolution X-ray results revealed that polar *c*-plane (0001), nonpolar *m*-plane (10-10) and *a*-plane (11-20) ZnO thin films were grown on *c*-plane, *m*- and *r*-sapphire substrates by atomic layer deposition, respectively. Compared with the *c*-plane ZnO film, nonpolar *m*-plane and *a*-plane ZnO films showed smaller surface roughness and anisotropic surface structures. Regardless of ZnO crystal planes, room temperature photoluminescence spectra represented two emissions which consisted of the near bandedge (~380 nm) and the deep level emission (~500 nm). The *a*-plane ZnO films represented better optical and electrical properties than *c*-plane ZnO, while *m*-plane ZnO films exhibited poorer optical and electrical properties than *c*-plane ZnO.

1. Introduction

Zinc oxide (ZnO) semiconductor has attracted much attention for optoelectronic materials such as light emitting diodes (LEDs) and transparent conducting oxide (TCO), etc. Due to its wide band gap(~3.37 eV at room temperature) and large exciton binding energy of ~ 60 meV, ZnO becomes an excellent semiconductor material for optoelectronic applications as a substitute of GaN. ZnO films have been usually grown on *c*-plane (0001) sapphire, where the ZnO films have (0001) orientation in the growth direction due to the minimum surface free energy of ZnO (0001) plane [1]. In this case, the electric field is polarized along the *c*-axis of wurtzite structures, resulting in the spontaneous and the piezoelectric polarizations. Therefore, it has been studied to grow nonpolar and semipolar ZnO thin films without the polarized electric field for the achievement of high efficiency nonpolar ZnO-based light emitting diodes and its applications. There are several reports on the growth of nonpolar *a*-plane (11-20) ZnO on *r*-plane sapphire substrates and *m*-plane (10-10) ZnO on *m*-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) [2–8]. In addition, a few studies have reported that nonpolar ZnO films were grown on *m*-sapphire [9] and p-Si (111) [10] by using atomic layer deposition (ALD).

ALD is one of the promising deposition techniques since it has several practical advantages including high accuracy, simple thickness control, large capability, good conformity and reproducibility [11]. In addition, ALD growth temperature of nonpolar ZnO was much lower than MOCVD, MBE and sputter, which would be advantageous to low temperature process for nonpolar GaN-based LEDs as nonpolar ZnO TCO material. However, their efforts to grow nonpolar ZnO films grown by ALD are limited to the characterization of crystallographic properties. In this study, we investigated the comprehensive characterization of polar and nonpolar ZnO grown on different sapphire substrates, and the effect of the growth temperature on the optical and electrical properties of polar and nonpolar ZnO grown by using the ALD system.

2. Experimental details

ZnO films of 100 nm-thick polar *c*-plane (0001), nonpolar *a*-plane (11-20) and *m*-plane (10-10) were grown on *c*-, *r*- and *m*-plane sapphire substrates by using an ALD technique, respectively. Diethylzinc [DEZn, $Zn(C_2H_5)_2$] with 6 N purity and distilled water (H_2O) were used as precursors of Zn and O, respectively. DEZ and H_2O were fed into the chamber through separate inlet lines and purged by N_2 gas in an ALD cycle. The opening and the closing sequences of the valves were controlled by a computer. The reactants were supplied by the pulse flow sequence of DEZn—N_2 purge–H_2O–N_2 purge. The exposure time of DEZn and H_2O was 1.0 s and the N_2 purging flow rate was fixed at 1600 sccm for 5 s. The growth temperatures of ZnO were 115 °C, 155 °C and 195 °C.

The crystal quality and the orientations of ZnO films were measured by high resolution X-ray diffraction (HR-XRD) ω-2θ scans using a PANalytical four circle X'Pert MRD X-ray diffractometer with a Cu-Kα radiation source (1.54 Å). Furthermore, the thickness of the ZnO film was measured by X-ray reflectivity. Surface morphology and root mean square (RMS) roughness of the grown ZnO films were investigated by atomic force microscope (AFM) with a non contact mode (NANOFOCUS my scope plus). We carried out room temperature photoluminescence (PL) to observe the optical properties of polar and nonpolar ZnO thin

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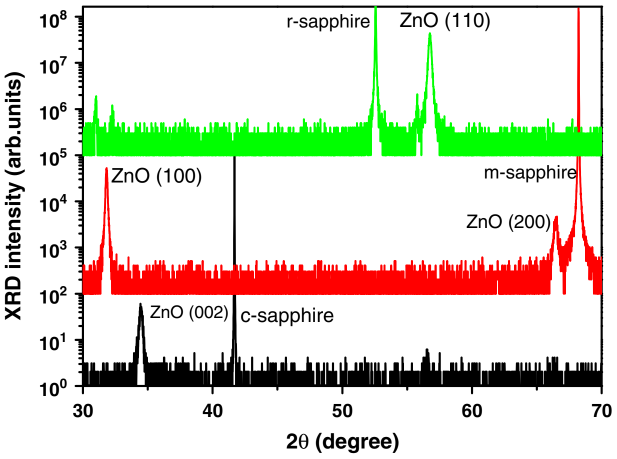

Fig. 1. HR-XRD $\omega/2\theta$ scans of *c*-plane, *a*-plane and *m*-plane ZnO films grown on *c*-plane, *r*-plane and *m*-plane sapphire substrates, respectively. The ALD growth temperature was 195 °C.

films such as bandedge emission and impurity-related green emission. For PL measurements, samples were focused by the 325 nm line of the He–Cd laser with the beam diameter of 20 μm and the excitation power of 1.0 kW/cm^2. All samples were analyzed by van der Pauw method to estimate the electrical properties of polar and nonpolar ZnO grown on different sapphire substrates using the room temperature Hall measurement system (ECOPIA HMS-3000).

3. Results and discussion

Fig. 1 showed the XRD $\omega/2\theta$ scans of polar (0001), nonpolar *a*-plane (11-20) and *m*-plane (10-10) ZnO films grown on *c*-plane, *r*-plane and *m*-plane sapphire substrates, respectively, at the growth temperature of 195 °C. As shown in Fig. 1, ZnO film deposited on *c*-plane sapphire represented ZnO reflection at 34.4° which was consistent with polar (0002) ZnO plane. In addition, ZnO films deposited on *m*-plane and *r*-plane sapphire substrates showed ZnO reflections at 31.7° and 56.6°, respectively. Both peaks at 31.7° and 56.6° were indexed as (10-10) and (11-20) of the wurtzite structure of ZnO. It implied that the ZnO films grown on *m*-plane and *r*-plane sapphire substrates represented single phased- and oriented-nonpolar *m*-plane and *a*-plane ZnO epilayers, respectively. From these results, we believed that the crystal orientations of ZnO films would be directly controlled by those of sapphire substrates.

Fig. 2(a), (b) and (c) showed the XRD $\omega/2\theta$ scans of *c*-plane, *m*-plane and *a*-plane ZnO films grown on *c*-, *m*-, and *r*-plane sapphire with different growth temperatures, respectively. XRD peak intensities of *c*-plane and *m*-plane ZnO films grown at 115 °C were lower than that of the *a*-plane ZnO film as shown in the inset of Fig. 2(d). However, XRD intensities of three samples were increased with the growth temperature. It indicated that the crystallinity of *a*-plane ZnO film would be better than that of the *c*-plane and *m*-plane ZnO films at the low growth temperature of 115 °C. In addition, we measured the grain sizes of *c*-plane and *a*-plane and *m*-plane ZnO films from the Scherrer's equation $D\ (\mathrm{nm}) = (k\lambda)/(\beta\cos\theta)$, where k is a constant, λ is the wavelength, β is the full width at half maxima (FWHM), and θ is the peak angle. Regardless of the crystallographic orientations of ZnO film, the grain sizes were increased with growth temperature as shown in Fig. 2(d). It indicated that the lateral growth of ZnO was improved with increasing growth temperature.

Fig. 3 (a), (b) and (c) showed the AFM images (1.0 × 1.0 μm) of *c*-plane, *m*-plane and *a*-plane ZnO films grown at the growth temperature of 195 °C, respectively. The surface morphologies of *c*-plane, *m*-plane and *a*-plane ZnO films represented small islands surface structures. It implied that ZnO films would still be 3-D growth mode in our experimental regions regardless of crystallographic planes. However, surface island structure was conglomerated and became bigger with increasing the growth temperature not shown in here. In addition, we believed

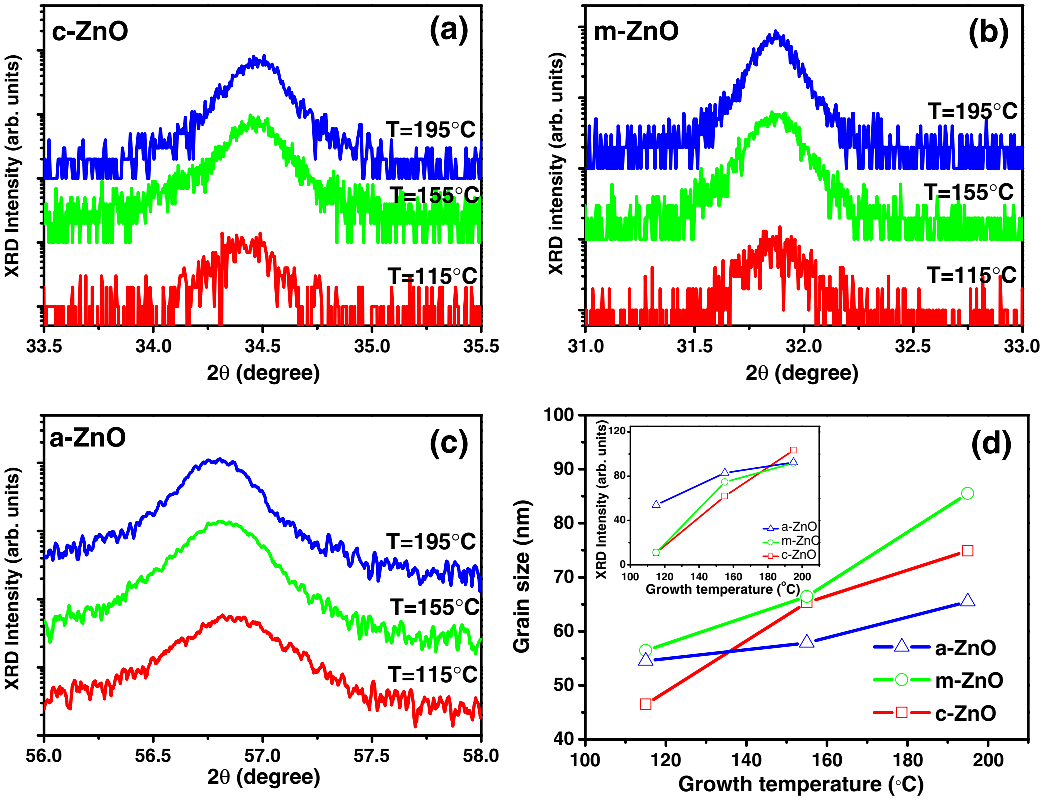

Fig. 2. HR-XRD $\omega/2\theta$ scans of *c*-plane (a), *m*-plane (b) and *a*-plane (c) ZnO films grown with different growth temperatures of 115 °C, 155 °C and 195 °C. Grain size (d) of ZnO films obtained from Scherrer's equation as a function of growth temperature and inset showed XRD intensity of ZnO films as a function of growth temperature.