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ScienceDirect
Journal of Crystal Growth 298 (2007) 472–476
JOURNAL OF CRYSTAL GROWTH
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Atomic layer deposition of epitaxial ZnO on GaN and YSZ

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Available online 14 December 2006

Abstract

ZnO thin films were epitaxially grown by atomic layer deposition on both of GaN/c-sapphire and yttria-stabilized zirconia (YSZ) substrates for comparison. X-ray diffraction, cross-sectional transmission electron microscopy (TEM) and photoluminescence (PL) measurements show that epitaxial ZnO films have better structural qualities and optical properties on GaN than on YSZ, whereas atomic force microscopy (AFM) shows that the surface of ZnO films on YSZ is smoother than on GaN. From the ZnO thickness measured by TEM, the growth rate of ZnO on GaN is about one (0 0 0 2) monolayer per cycle, which is roughly four times of that on YSZ.

PACS: 68.55.Ac; 81.15

Keywords: A1. Interfaces; A3. Atomic layer epitaxy; B1. Oxides; B2. Semiconducting II–VI materials

1. Introduction

Direct wide band gap ZnO semiconductor is an attractive material for optoelectronic devices because it has a high exciton binding energy (60 meV) that can result in efficient light emission. To attain the high-performance ZnO-based optoelectronic devices, it is necessary to prepare high-quality epitaxial ZnO thin films. Among various methods for epitaxy of ZnO films, atomic layer deposition (ALD) is attractive as it can deposit a film in a surface-controlled manner with layer-by-layer growth that is desirable for multi-quantum well structures [1]. Other advantages of ALD include uniformity with large areas, good reproducibility, multilayer processing capability, and high-quality films at relatively lower temperature [2]. Although ZnO deposition by ALD has been developed in early beginning of ALD in 1980s, epitaxial growth of ZnO has received relatively less attention [3,4].

Because GaN and ZnO have similar lattice constants (1.8% mismatch) and a small difference of the in-plane linear thermal expansion coefficient [5], GaN is a suitable substrate on which epitaxial ZnO can easily grow. Thus, optimization of ALD conditions for ZnO epitaxial growth can be experimentally found without much difficulty [3,6]. Also, yttria-stabilized zirconia YSZ (1 1 1) single-crystal substrate which has a lattice mismatch of about 10% with ZnO [7], is used for comparison with GaN substrate. YSZ has a CaF_2-type cubic structure with a lattice parameter about 0.514 nm. Ohta et al. [8] demonstrated that high-quality ZnO epitaxial layers can be grown on YSZ substrates by a pulsed-laser deposition technique. However, there has been no report to grow ZnO films on YSZ substrates by ALD so far.

2. Experimental procedure

Atomic layer deposition of ZnO films on epi-GaN/sapphire and YSZ (1 1 1) substrates was carried out using diethylzinc (DEZn) and H_2O as zinc and oxygen precursors in reservoirs at 22 °C, respectively. GaN substrates were grown on 2-in diameter sapphire by metalorganic chemical vapor deposition. ALD was carried out in a commercial flow type F-120 (Microchemistry Ltd., Finland) reactor at

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doi:10.1016/j.jcrysgro.2006.10.139

a pressure of 6–8 Torr during deposition. The pulse period was 0.5–5 s for the precursors and 1–5 s for the purge time between the reactants. The purging N_2 gas flow rate was 500 sccm. In our experiments, the zinc source was first supplied on the substrate surface. Before deposition on YSZ and GaN substrates, we used Si substrate to determine the ALD processing window in which it exhibited the ALD self-limiting characteristics. Therefore, the substrate temperature range of 200–300 °C was used for ZnO deposition. The GaN substrates had been cleaned by ethanol and acetone before deposition of ZnO. Also, on the YSZ substrates ($1 \times 1\,cm^2$) the particles and organic contaminants had been removed using acetone and methanol solution. No further pretreatment on the substrates were carried out after loading into the reactor.

Crystalline quality and orientations of ZnO films were evaluated by X-ray diffraction (XRD), surface morphologies were examined by atomic force microscopy (AFM), and photoluminescence (PL) spectra were measured at room temperature. The thickness and interfacial microstructures of films were observed using cross-sectional transmission electron microscopy (TEM).

3. Results and discussion

In Fig. 1(a), the XRD pattern from a ZnO film on GaN deposited for 700 cycles shows only (0 0 0 2) peaks, implying that basal planes of ZnO are parallel to the GaN substrate surface. Fig. 1(b) is a X-ray rocking curve of ZnO (0 0 0 2) reflection with the full-width at half-maximum (FWHM) value of 324 arcsec. This FWHM value is slightly better than other reported data for ZnO epi-layers grown on GaN substrate by ALD [3], indicating that the film is of good structural quality. In contrast, when we directly deposited on sapphire in similar experimental conditions, it was found no epitaxy of ZnO. From the (0 0 0 2) peak width in Fig. 1(a), the grain size is estimated, using Scherrer's formula, to be about 90 nm. Fig. 1(c) is the XRD pattern of a ZnO film deposited on YSZ substrate by ALD in the same deposition condition. On YSZ, it is also found that ZnO only shows (0 0 0 2) and (0 0 0 4) peaks with the FWHM value of 0.25° for (0 0 0 2) reflection. The estimated grain size is thus about 40 nm, which is much smaller than that on GaN substrate.

The surface morphologies of ZnO on GaN and YSZ substrates deposited at 300 °C are shown in AFM images of Figs. 2(a) and (b), respectively. The root mean square (rms) surface roughness of the ZnO films on GaN and YSZ substrates is about 4.6 and 1.9 nm, respectively. For longer pulse time, the surface roughness increases to 5.9 nm. When the YSZ substrate temperature was at 275 °C, the surface roughness is slightly reduced to 1.6 nm. From the AFM images, the averaged grain size of ZnO films on YSZ and

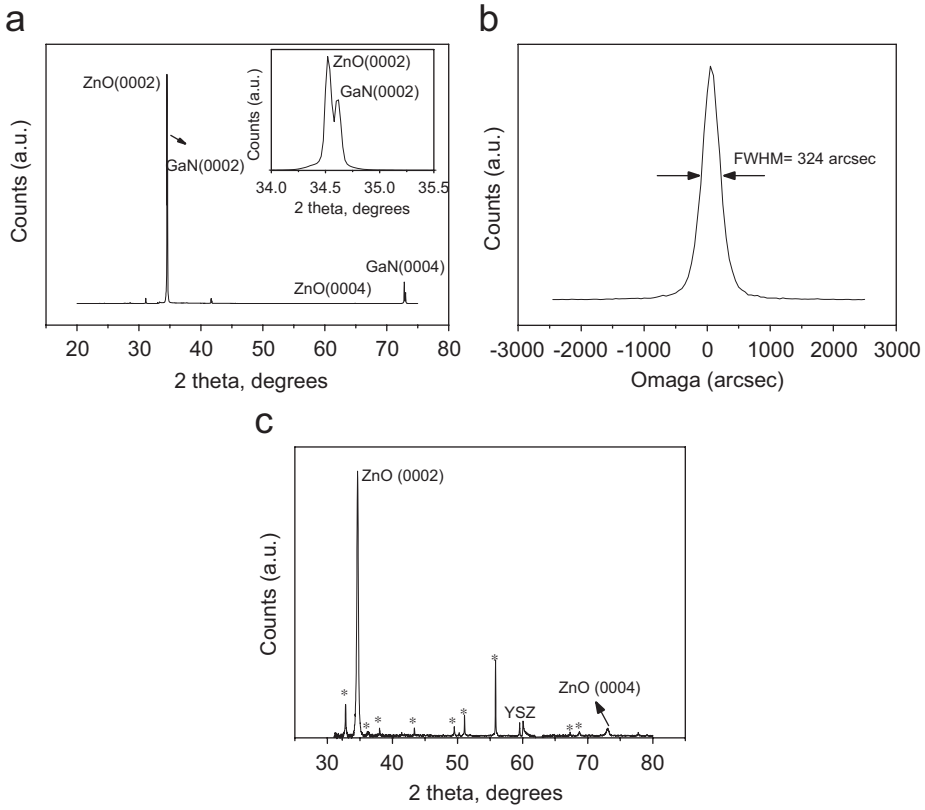

Fig. 1. (a) θ–2θ XRD pattern of ZnO on GaN. The inset is the enlargement of ZnO and GaN (0 0 0 2) peaks; (b) (0 0 0 2) rocking curve of ZnO on GaN; (c) θ–2θ XRD pattern of ZnO on YSZ. The peaks marked with * are reflections from ZnO and YSZ due to the Cu–Kβ, Ni–Kα and *W*-Lα_1 radiations from a contaminated X-ray source.

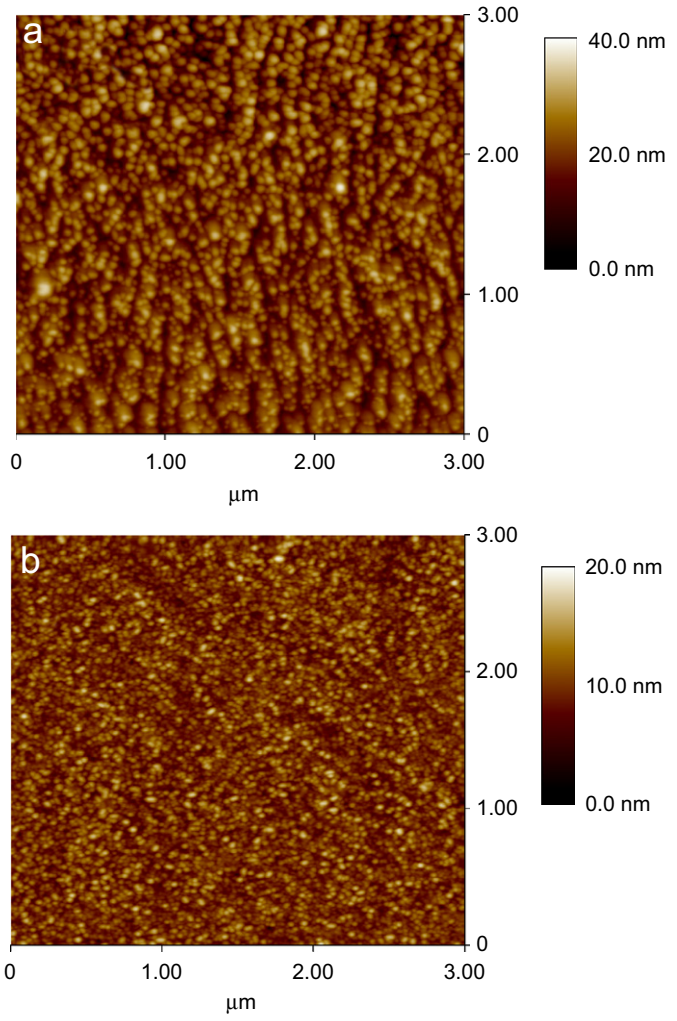

Fig. 2. AFM images of ZnO grown on (a) GaN and (b) YSZ.

GaN is approximately 38 and 90 nm, which are consistent with the data from XRD evaluation.

Fig. 3 shows the room temperature PL spectra of ZnO thin films grown on GaN and YSZ substrates by ALD. On the GaN substrate, PL in Fig. 3(a) shows a sharp peak of UV emission at 3.24 eV with the FWHM of about 127 meV. The green emission was hardly observed from the ZnO/GaN sample. On YSZ, we can also see a sharp peak at the energy of 3.24 eV indicating UV light emission as shown in Fig. 3(b). The FWHM of the UV emission peak is about 150 meV which is larger than that on GaN. However, there is a broad peak around the energy of 2.4 eV corresponding to green and yellow emissions. It is believed that they may originate from defects of the thin films such as either oxygen vacancies or interstitial zinc ions. The ratio of UV/green emission intensities is nearly 1.1. This result suggests that it might not form perfect Zn–O bonds at each growth cycle and contain some Zn–Zn bonds in the thin film [4]. Compared with the ZnO/YSZ sample, the negligible green emission from ZnO on GaN suggests a lower density of defects in the ZnO layer.

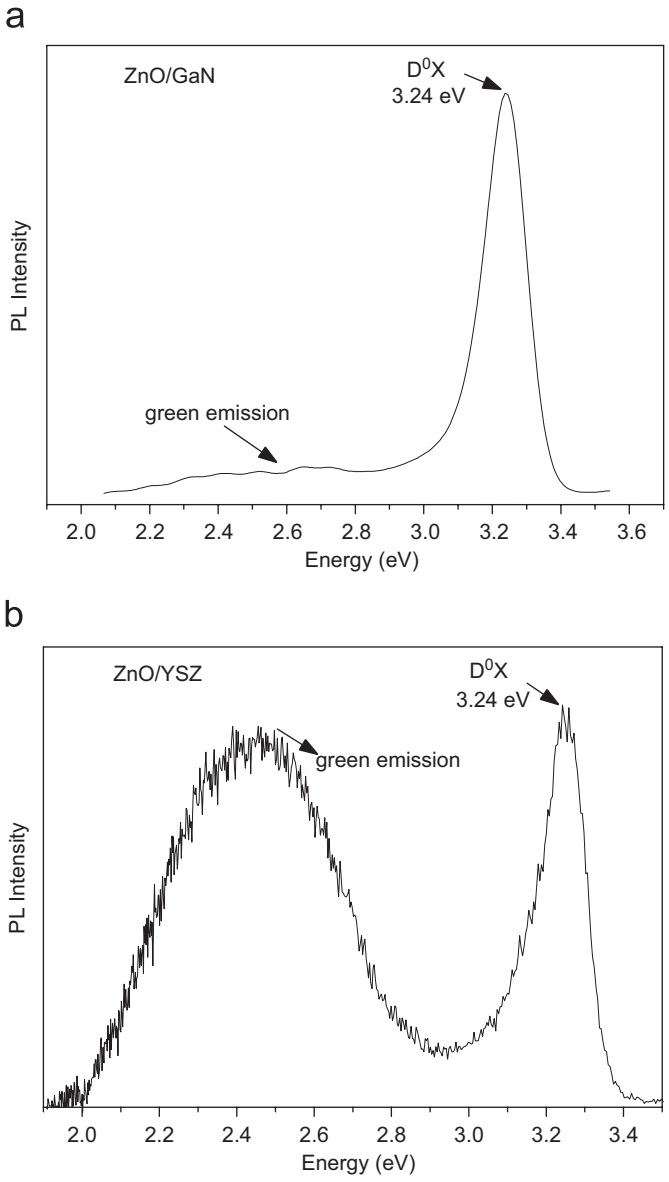

Fig. 3. Room-temperature PL spectra of ZnO layers grown on (a) GaN and (b) YSZ.

Fig. 4(a) is a bright-field TEM image for ZnO on GaN substrate. The ZnO thin film is a highly *c*-axis oriented layer from the analysis of the selected area diffraction (SAD) pattern as shown in Fig. 4(b). The SAD pattern is obtained from both the ZnO layer and GaN substrate. The orientation relationship between ZnO and GaN is determined to be $(0\,0\,0\,2)_{ZnO}||(0\,0\,0\,2)_{GaN}$ and $[2\,\bar{1}\,\bar{1}\,0]_{ZnO}||[2\,\bar{1}\,\bar{1}\,0]_{GaN}$. From the TEM image, the measured average thickness of ZnO layer on GaN is about 170 nm, and the growth rate is estimated to be 0.25 nm/cycle close to one monolayer of (0 0 0 2) basal plane. Kaiya et al. [9] reported similar results that the growth rate of epitaxial ZnO films deposited on sapphire at 450–550 °C by ALD was 0.26 nm close to a half of the *c*-axis lattice parameter of hexagonal ZnO crystal. A cross-sectional bright-field TEM micrograph of ZnO on YSZ is shown in Fig. 4(c), and the SAD

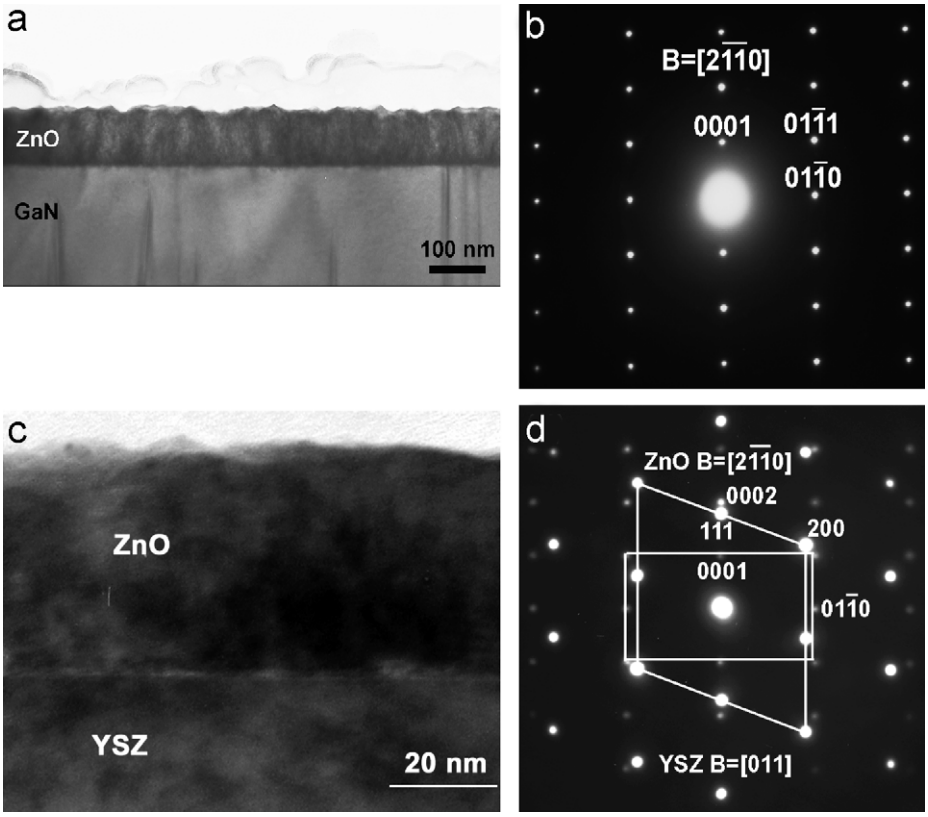

Fig. 4. (a) Cross-sectional bright-field TEM image of ZnO on GaN and (b) the corresponding electron diffraction pattern in [2 $\bar{1}$ $\bar{1}$ 0] zone axis. (c) Cross-sectional bright-field TEM image of ZnO on YSZ and (d) the corresponding electron diffraction pattern in [1 1 0] zone axis of YSZ.

pattern in Fig. 4(d). It can be seen the thickness of the ZnO film is uniform in about 45 nm, which gives the averaged growth rate of 0.07 nm/cycle roughly about 1/4 of ZnO (0 0 0 2) interplanar spacing. From the SAD pattern, the orientation relationship between ZnO and YSZ can be determined as $(0\,0\,0\,2)_{ZnO}||(1\,1\,1)_{YSZ}$ and $[2\,\bar{1}\,\bar{1}\,0]_{ZnO}||[1\,\bar{1}\,0]_{YSZ}$. Compared with ZnO on YSZ, the growth rate of ZnO grown on GaN in the same experimental condition is much higher. The reason could be due to large lattice mismatch of ZnO with YSZ, which could strain the initially deposited ZnO. As a result, it might retard the nucleation of ZnO due to the activation energy barrier. Yousfi et al. [10] reported in their ALD study that an induction period was observed for ZnO nucleation on Au substrate. Another speculation is that the water vapor as the oxygen source during deposition can easily diffuse into YSZ, resulting in insufficient adsorption of O–H species to form complete Zn–O bonds. This might also induce formation of defects to cause the strong green emission in the PL spectra.

Fig. 5 is a cross-sectional high-resolution TEM image of the interface between ZnO and GaN along the [1 1 $\bar{2}$ 0] direction. As seen from the (0 0 0 2) lattice fringes, it reveals that the interface is sharp and smooth without the formation of any interlayer, which is similar to our previous TEM observations of MOCVD ZnO on GaN [11] and others on the study of MBE growth of ZnO on GaN [12,13]. In contrast, Hong et al. [12] shown in their study of deposition of ZnO by molecular beam epitaxy that there is an interfacial layer between ZnO and Ga-polar GaN. Also, the good coherency of ZnO and GaN layers across the interface can be clearly seen.

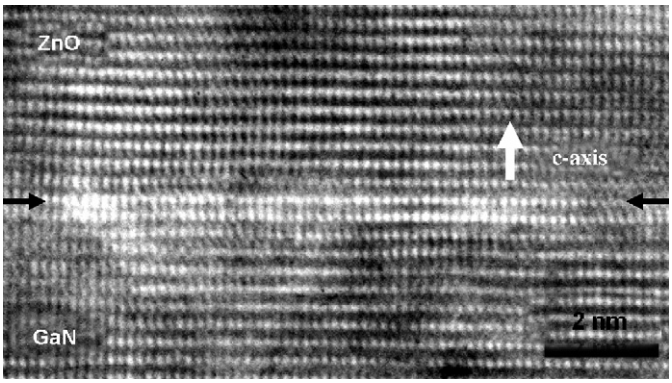

Fig. 5. (a) HRTEM image of the interfacial region between ZnO and GaN viewed along the [2 $\bar{1}$ $\bar{1}$ 0] zone axis. The black arrows indicate the position of the interface.

In summary, epitaxial ZnO thin films with good structural qualities were successfully deposited on GaN and YSZ substrates at 300 °C by atomic layer deposition. The growth rate is approximately one monolayer of

(0 0 0 2) plane per cycle on GaN, whereas it is much less than one monolayer on YSZ. The interface between ZnO and GaN is atomically sharp with good coherency.

Acknowledgment

Part of the work was supported by National Science Council, Taiwan, ROC, under contracts NSC 94-2216-E-009-024.

References

[1] R. Triboulet, J. Perrie‘re, Prog. Crystal Growth Character. Mater. 47 (2003) 65–138.
[2] M. Ritala, Appl. Surf. Sci. 112 (1997) 223.
[3] K. Saito, K. Nagayama, Y. Hosokai, K. Ishida, K. Takahashi, Phys. Stat. Sol. c 1 (2004) 969.
[4] J.M. Lim, K.C. Shin, H.W. Kim, C.M. Lee, J. Lumin. 109 (2004) 181.
[5] B.M. Ataev, W.V. Lundin, V.V. Mamedov, A.M. Bagamadova, E.E. Zavarin, J. Phys.: Condens. Matter 13 (2001) L211.
[6] K. Kopalko, M. Godlewski, J.Z. Domagala, E. Lusakowska, R. Minikayev, W. Paszkowicz, A. Szczerbakow, Chem. Mater. 16 (2004) 1447.
[7] K. Nomura, et al., J. Appl. Phys. 95 (10) (2004) 5532.
[8] H. Ohta, H. Tanji, M. Orita, H. Hosono, H. Kawazoe, Mater. Res. Soc. Symp. Proc. 570 (1999) 309.
[9] K. Kaiya, N. Yoshii, K. Omichi, N. Takahashi, T. Nakamura, S. Okamoto, H. Yamamoto, Chem. Mater. 13 (2001) 1952.
[10] E.B. Yousfi, J. Fouache, D. Lincot, Appl. Surf. Sci. 153 (2000) 223.
[11] W.C. Hou, et al., Phys. Stat. Sol. c 1 (2004) 856.
[12] S.K. Hong, T. Hanada, H.-J. Ko, Y. Chen, Ta. Yao, D. Imai, K. Araki, M. Shinohara, K. Saitoh, M. Terauchi, Phys. Rev. B 65 (2002) 115331.
[13] M. Abouzaid, P. Tailpieda, P. Ruteranaa, C. Liub, B. Xiaob, S.-J. Chob, Y.-T. Moonb, H. Morkoçb, Superlattices Microstruct. 39 (2006) 387.