Available online at www.sciencedirect.com
ScienceDirect
Journal of Crystal Growth 298 (2007) 461–463
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Growth of epitaxial ZnO thin film on yttria-stabilized zirconia single-crystal substrate

Yen-Cheng Chao[a], Chih-Wei Lin[a], Dong-Jie Ke[a], Yue-Han Wu[a], Hou-Guang Chen[a], Li Chang[a,*], Yen-Teng Ho[a,b], Mei-Hui Liang[a,c]

[a]*Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan*
[b]*Chung-Shan Institute of Science and Technology, Longtan, Taoyuan, Taiwan*
[c]*Center of General Education, Chung-Hua University, Hsinchu 300, Taiwan*

Available online 18 December 2006

Abstract

ZnO growth on yttria-stabilized zirconia (YSZ) (1 1 1) single-crystal substrate has been carried out by metalorganic chemical vapor deposition (MOCVD). High-quality epitaxial ZnO has been evidenced by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Cross-sectional TEM from all deposited films reveals that the interface between ZnO and YSZ is atomically flat, and orientation relationship is deduced to be $[1\,\bar{1}\,0\,0]_{ZnO}//[1\,1\,\bar{2}]_{YSZ}$, $[2\,\bar{1}\,\bar{1}\,0]_{ZnO}//[0\,1\,1]_{YSZ}$ and $(0\,0\,0\,2)_{ZnO}//(1\,1\,1)_{YSZ}$. It has been found that surface roughness increases with the substrate temperature in the range of 500–700 °C. The growth rate also varies with the temperature.

PACS: 68.55.Ac; 81.15; 68.37

Keywords: A1. Interfaces; A3. Metalorganic chemical vapor deposition; B1. Oxides; B2. Semiconducting materials

1. Introduction

Epitaxial growth of ZnO has been attracting interest as active materials in optoelectronics in recent years [1–3]. Though ZnO has been prepared by various deposition methods on a wide range of substrates, it is still a challenge for obtaining high-quality epitaxial films by chemical vapor deposition (CVD). Here, we report that it is possible to deposit high-quality ZnO films on yttria-stabilized zirconia (YSZ) (1 1 1) substrates. YSZ has the CaF_2-type cubic structure (space group Fm3m) with lattice parameter of 0.514 nm which gives about 10% lattice mismatch with ZnO. The advantages for using YSZ as substrate for CVD include the followings: relatively-low cost single-crystal wafers are commercially available; it is thermally and chemically stabilized without any reaction with ZnO at temperature below 1200 °C; and an atomically smooth surface can be easily obtained. Epitaxial growth of ZnO on YSZ has been demonstrated by a pulsed-laser deposition technique [4]. However, there has been no report for deposition of epitaxial ZnO on YSZ by metalorganic chemical vapor deposition (MOCVD).

2. Experimental procedure

Deposition of ZnO was carried out in a vertical tube furnace at atmospheric pressure. We used zinc acetylacetonate ($Zn(C_5H_7O_2)_2$) as the Zn source to benefit from its low cost and easiness to handle [5]. The precursor of zinc acetylacetonate in solid powders was heated at 130–132 °C and N_2 gas was used as carried gas. The O_2 gas was separately flowed into the furnace. The substrate temperature was in the range of 450–700 °C. YSZ (1 1 1) substrate in $1 \times 1\,cm^2$ size was cleaned by acetone before deposition. The surface roughness (rms) of as-received YSZ substrates by atomic force microscopy (AFM) is less than 0.2 nm. X-ray diffraction (XRD) and transmission electron

*Corresponding author. Tel.: +886 3 5731615; fax: +886 3 5724727.
E-mail address: lichang@cc.nctu.edu.tw (L. Chang).

0022-0248/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2006.10.165

microscopy (TEM) were performed for structural characterization. Surface morphologies were done by AFM and scanning electron microscopy (SEM). Photoluminescence (PL) and Hall measurements were carried out for the evaluation of optical and electrical properties.

3. Results and discussion

In the XRD pattern (Fig. 1) only ZnO basal plane reflections can be seen, indicating that (0 0 0 2) planes of ZnO are parallel to the YSZ(1 1 1) surface. The grain size is estimated, using the Scherrer's formula, to be 50 nm. The (0 0 0 2) X-ray rocking curve shows the full-width at half-maximum value of 133 arcsec, approaching the reported value of 100 arcsec for ZnO homoepitaxy by MOCVD [6]. Thus, it suggests that a high-quality ZnO film can be deposited on YSZ. There is no apparent difference among the XRD patterns from ZnO formed at different temperature in all of which ZnO shows only the (0 0 0 2) and (0 0 0 4) peaks. AFM shows that the surface roughness can be 0.7 nm for films deposited at 500 °C as seen in Fig. 2(a). However, the roughness increases with the substrate temperature. For the film grown at 700 °C, SEM shows that the surface becomes rough and the grain size is increased to 160 nm. A typical electron diffraction pattern for all ZnO formation at the deposition temperature from 500–700 °C in this study is shown in Fig. 3(a) and (b). The orientation relationship between ZnO and YSZ is determined to be $(0\,0\,0\,2)_{ZnO}//(1\,1\,1)_{YSZ}$ and $[1\,1\,\bar{2}\,0]_{ZnO}//[1\,\bar{1}\,0]_{YSZ}$. From Fig. 3(a) which shows $(1\,1\,\bar{2}\,0)_{ZnO}//(2\,2\,0)_{YSZ}$, the in-plane mismatch can be deduced to be about 10% as expected from the crystal lattices of ZnO and YSZ. In the cross-sectional TEM micrograph (Fig. 3(c)), a smooth ZnO film on YSZ deposited at 500 °C can be observed over the imaged region, and the film thickness is approximately 120 nm. For 600 °C deposition, TEM (not shown) shows a relative rough but thicker film. The growth rate determined from TEM is then 4 nm/s for 500 °C and 13 nm/s for 600 °C. Though the columnar structure is clearly seen in the TEM for the cases of both deposition temperatures, the SAD pattern exhibits single-crystalline characteristics. The lattice image of an interfacial region between ZnO and YSZ in $[1\,\bar{1}\,0\,0]$ is shown in Fig. 4. It is readily observed that no interfacial layer exists, and the interface is quite flat. The (0 0 0 2) planes of ZnO are parallel to the (1 1 1) planes of YSZ as seen from the lattice fringes and the corresponding fast-Fourier-transform

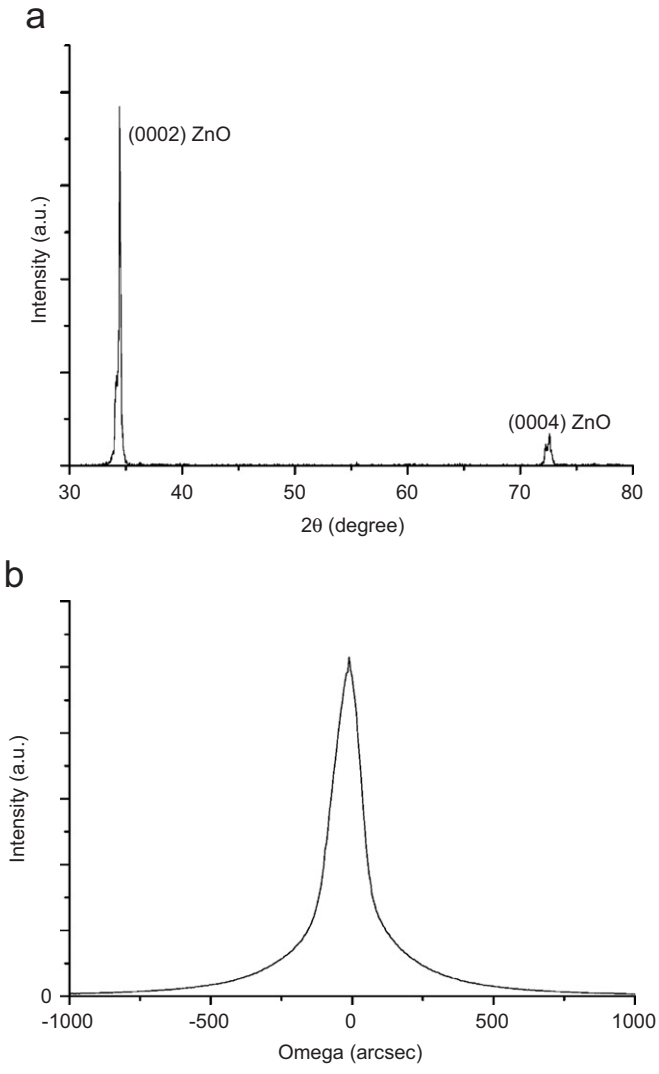

Fig. 1. (a) θ–2θ scan XRD pattern of ZnO deposited at 600 °C and (b) the rocking curve (ω scan) for (0 0 0 2) peak.

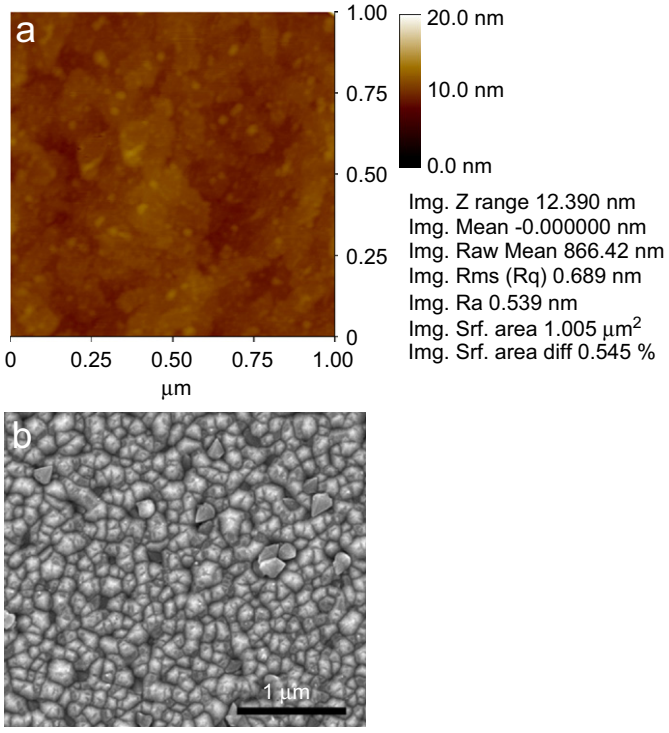

Fig. 2. (a) AFM image of the surface of a ZnO film deposited at 500 °C and (b) SEM image of the surface deposited at 700 °C.

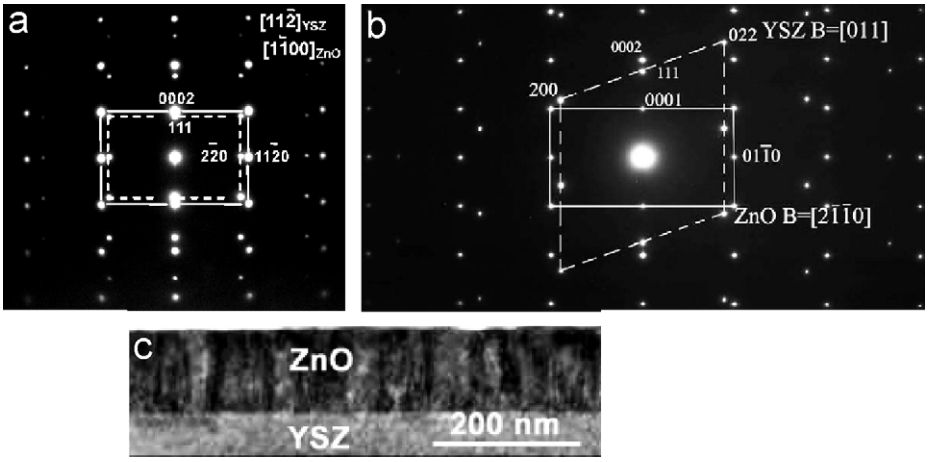

Fig. 3. (a) and (b) SAD patterns from a cross-sectional TEM sample as shown in the bright-field image in (c) ZnO growth temperature was 500 °C.

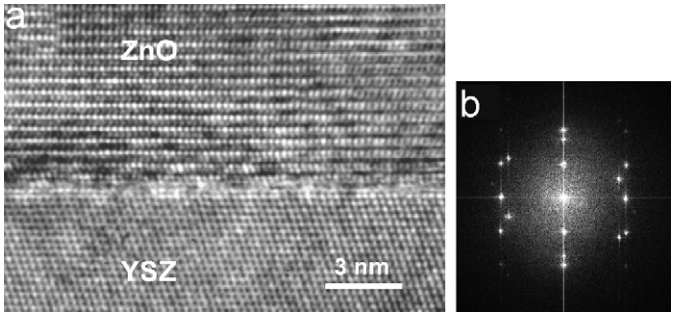

Fig. 4. (a) HRTEM of ZnO on YSZ showing the interface and (b) the corresponding fast-Fourier-transform pattern.

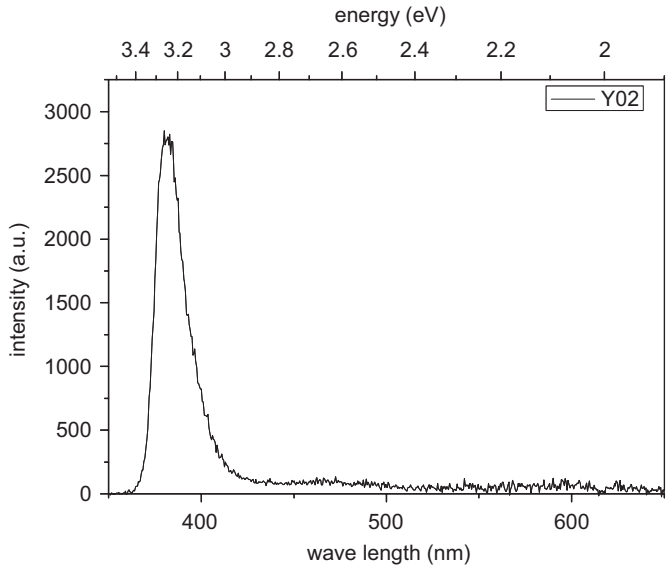

Fig. 5. PL spectrum obtained at room temperature from ZnO deposited at 600 °C.

pattern shown in Fig. 4(b). The coherency across the interface is as expected from the crystal symmetry of 3 m of both oxides.

Further, we measured the film properties based on PL and Hall measurements. The PL spectrum at room temperature from ZnO deposited at 600 °C shows clearly the strong UV emission at 3.25 eV with a negligible intensity from green emission as shown in Fig. 5. For 700 °C deposition, a high intensity of green emission is excited from the ZnO film which may contain more defects. The Hall measurements give the electron mobility in the range of 20–25 $cm^2/V\,s$ which is observed to be independent of deposition temperature.

In summary, high-quality epitaxial ZnO films can form on YSZ(1 1 1) by atmospheric MOCVD. An atomically smooth interface with good coherency between ZnO and YSZ is observed. The surface roughness increases with deposition temperature.

Acknowledgment

This work was supported by National Science Council, Taiwan, ROC, under Contract NSC 94-2216-E-009-024.

References

[1] R. Triboulet, J. Perrie're, Prog. Cryst. Growth Charact. Mater. 47 (2003) 65.
[2] S.J. Pearton, D.P. Nortona, K. Ipa, Y.W. Heoa, T. Steiner, Prog. Mater. Sci. 50 (2005) 293.
[3] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, H. Morkoç, J. Appl. Phys. 98 (2005) 041301.
[4] K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Orita, M. Hirano, J. Appl. Phys. 95 (2004) 5532.
[5] Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi, H. Watanabe, J. Crystal Growth 221 (2000) 431.
[6] T. Gruber, C. Kirchner, A. Wagg, Phys. Stat. Sol. (b) 229 (2002) 841.