Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 2259–2262

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Heteroepitaxial ZnO/sapphire (0 0 0 1) structure prepared by sol–gel process

Kyu-Seog Hwang [a], Bo-An Kang [a], Yu-Sang Kim [b], Seung Hwangbo [c], Jin-Tae Kim [d,*]

[a] Department of Biomedical Engineering, Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, Republic of Korea
[b] Korea Institute of Science and Technology Information, 66 Hoegiro, Dongdaemun-gu, Seoul 130-741, Republic of Korea
[c] Department of Electronic and Photonic Engineering, Honam University, 59-1 Seobong-dong, Gwangsan-gu, Gwangju 506-714, Republic of Korea
[d] Department of Photonic Engineering, College of Engineering, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501-759, Republic of Korea

Received 5 February 2010; received in revised form 29 March 2010; accepted 22 May 2010
Available online 25 June 2010

Abstract

ZnO thin films were grown on sapphire (0 0 0 1) substrates by sol–gel process and their structural and optical properties were characterized in detail. High-quality texture was obtained by using precursor solution of zinc acetate and ethanolamine in 2-methoxyethanol, pyrolyzed at 300 °C, then heated at 500 °C, and finally annealed at 750 °C. Highly *c*-axis oriented ZnO films were confirmed by X-ray θ–2θ scan. A relatively high transmittance in the visible spectra range and clear absorption edge of the film were observed. Epitaxial relationship between ZnO and sapphire and photoluminescence of the film were examined by using a X-ray pole-figure analysis and He–Cd laser. Near-band-edge emission with a deep-level emission was observed.

Keywords: A. Sol–gel; D. ZnO; Sapphire (0 0 0 1); Epitaxial relationship

1. Introduction

ZnO is both a piezo-electric and electro-optic (EO) material, and a semiconductor which possesses a wide band gap (3.2–3.3 eV) [1] so that it has been applied in wide range of applied fields. The most unique property of ZnO is its large exciton binding energy of 60 meV, which is much larger than those of GaN (24 meV), ZnSe (19 meV) and ZnS (39 meV) [2]. Owing to these properties, ZnO is considered to be a promising material for light-emitting devices and semiconductor lasers with low thresholds in the ultraviolet (UV) region.

For the realization of exciton-based photonic devices, high-quality epitaxial thin films are necessary. Different kinds of substrates were investigated for the high-quality epitaxial growth of ZnO film. Due to its physical, chemical and economical parameters, basal plane sapphire (SAP) has turned out to be most appropriate substrate. The high lattice mismatch (f_m) yields a large dislocation density and restricts the highly epitaxial film by chemical solution-based process, such as sol–gel. Sol–gel methods are being employed increasingly for the low-cost fabrication of ordered high-specification materials since structural and morphological characteristics may be tuned in order to tailor the optical or electrical properties of the materials. Although there have been several papers on the textured ZnO [2,3], it is very difficult to search previous works on the epitaxial growth of ZnO thin film on SAP single crystal prepared by sol–gel process.

In our previous works, epitaxial ZnO thin films on 6H-SiC (0 0 0 1) substrates were obtained by sol–gel process using a zinc-naphthenate precursor [4] and highly *c*-axis oriented ZnO films were successfully prepared on amorphous glass substrates with a zinc acetate – 2-methoxyethanol – 2-aminoethanol (MEA) solution [5]. The as-deposited film will sequentially pyrolyze and crystallize to ZnO during final annealing at >500 °C. In chemical solution-based process, removal of the solvent and the organics substances produced by acetate decomposition prior to crystallization may be the key factor that provides oriented crystal growth.

From Wessler's previous report [6] on textured ZnO films on sapphire (SAP) (0 0 0 1) produced by chemical solution deposition, precursor solutions as well as the heat-treatment parameters had a strong effect on the film microstructure. Although, however, crystallographical and structural properties

---

[*] Corresponding author. Tel.: +82 62 230 7019; fax: +82 62 230 7437.
E-mail address: kimjt@mail.chosun.ac.kr (J.-T. Kim).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.06.007

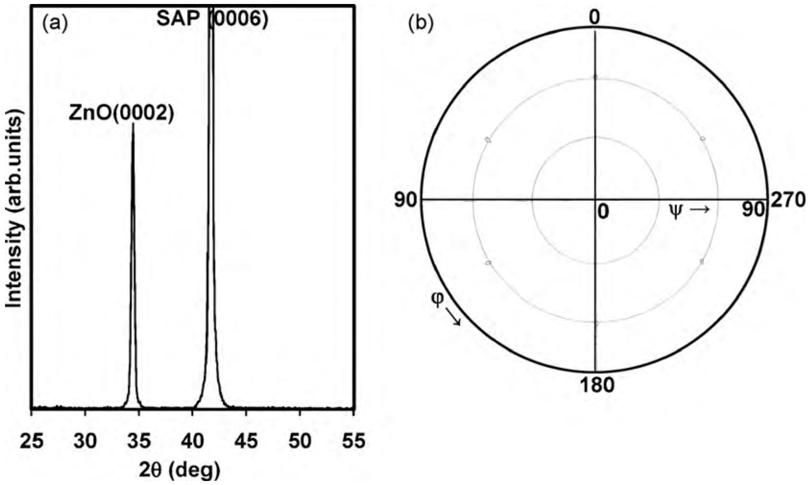

Fig. 1. XRD θ–2θ scan (a) and pole-figure analysis (b) of the finally annealed ZnO film on SAP (0 0 0 1) substrate.

of textured ZnO were fully discussed by using a X-ray diffraction (XRD) and transmission electron microscopy (TEM), optical properties was not presented.

In the present work, we prepared epitaxial ZnO thin films on SAP (0 0 0 1) substrate with a solution containing zinc acetate and MEA in 2-methoxyethanol as the solvent. We present structural, morphological and optical characterization of epitaxial ZnO film.

2. Experimental procedure

The experimental procedure and reagents used in this study were the same as those on the previous works [7]. Briefly, a homogeneous coating solution was prepared by mixing zinc acetate [$(CH_3COO)_2Zn\cdot 2H_2O$] and 2-methoxyethanol ($HOCH_2CH_2OCH_3$). MEA ($H_2HCH_2CH_2OH$) was added to obtain a clear sol (concentration: 0.6 mol Zn acetate/l 2-methoxyethanol). The molar ratio of MEA to Zn acetate was fixed at 1.0. The mixed solution was stirred for 2 h to obtain a homogeneous sol. SAP (0 0 0 1) wafer was washed in a H_2O_2 solution for 10 min at 25 °C, rinsed in de-ionized water and blown dry with N_2.

The starting sol was spin-coated onto the substrate at 2000 rpm for 10 s in air. The as-deposited film was pre-fired at 300 °C for 10 min in air. The second heating was performed in air at 500 °C for 1 h, and then finally annealed at 750 °C for 1 h in N_2. The thickness of the finally annealed ZnO film was about ~180 nm confirmed using reflection spectrum.

The crystallinity of the ZnO film was investigated by using a high resolution X-ray diffraction (HRXRD, X'Pert PRO, Philips, Netherlands). In-plane alignment of the film was examined by X-ray pole-figure analysis. Surface morphology and surface roughness of the film were observed by a scanning probe microscope (SPM, XE-200, PSIA, Korea). The transmittance in the visible range was measured using a UV–visible–NIR spectrophotometer (CARY 500 Scan, Varian, Australia). Room-temperature photoluminescence (PL) spectra were measured by micro-PL system (LabRamHR, Jobin Yvon, France) using 325 nm line of a He–Cd laser.

3. Results and discussion

Fig. 1(a) is a representative θ–2θ scan of the ZnO film grown on SAP (0 0 0 1) substrate. It exhibits the typical XRD peaks of the ZnO and SAP substrate to the (0 0 0 2) and (0 0 0 6) planes, respectively. These peaks indicate the c-axis oriented growth of the ZnO layer on the SAP substrate, *i.e.*, a growth along the c-axis. Using the SAP (0 0 0 6) peak as an internal calibration standard, the lattice constant of the substrate surface ($d_{\perp}$), which is perpendicular to the highly oriented ZnO films, was determined to be 5.2051 Å. The lattice constant of the ZnO film is slightly smaller than the value of the bulk crystal (5.2066 Å), possibly due to the tensile stress effect in the a- and b-axis from the lattice misfit between the ZnO film and SAP substrate. Considering the in-plane lattice parameter of SAP substrate ($a = 4.758$ Å) with respect to the ZnO layer ($a = 3.246$ Å), the amount of f_m can be calculated using the relation $f_m = [(a_l - a_s)/a_s] \times 100\%$, where a_l is the thin film and a_s is the substrate lattice constant [1]. The f_m value of ZnO/SAP heterostructure is estimated to be +18%. This f_m value indicates the tensile strain is active for the ZnO/SAP heterointerface.

Internal stress of ZnO film was calculated by biaxial stain model [5]. Film strain $\varepsilon = [(c_{film} - c_{bulk})/c_{bulk}]$ in the direction of the c-axis, *i.e.*, perpendicular to the substrate surface, was measured by using XRD. To drive the stress of the film parallel to the film's surface, we used the following formula [8], which is valid for a hexagonal lattice:

$$\sigma_{film} = \left[\frac{2c_{13}^2 - c^{33}(c_{11} + c_{12})}{2c_{13}}\right] \times \left[\frac{(c_{film} - c_{bulk})}{c_{bulk}}\right] \quad (1)$$

The elastic constant c_{ij} of single crystalline ZnO were used: $c_{11} = 208.8$, $c_{33} = 213.8$, $c_{12} = 119.7$, and $c_{13} = 104.2$ GPa [8]. The stress in the film (+0.0043), can be estimated using Eq. (1). The positive sign for the film after annealing at 750 °C indicates that the lattice constant c is constricted as compared to unstressed powder; therefore, the film is in a state of compression.

To investigate the in-plane alignment of this film, XRD pole-figure analysis was measured for the film heat-treated at 750 °C.

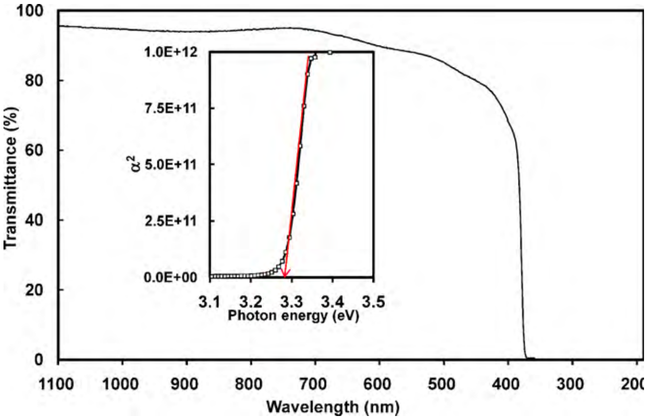

Fig. 2. UV–visible spectra of the finally annealed ZnO film on SAP (0 0 0 1) substrate. The inset shows plot of α^2 *vs.* $h\nu$.

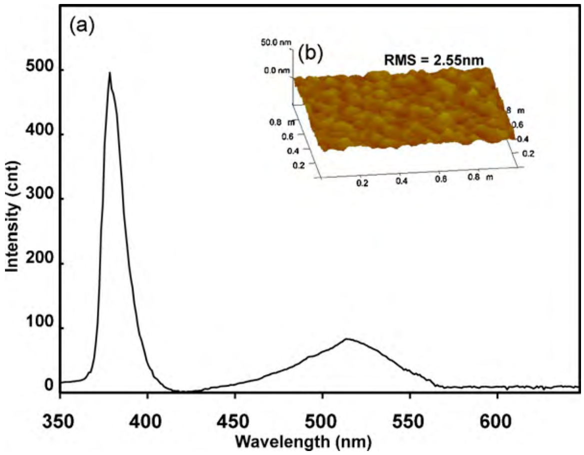

Fig. 3. PL spectra (a) and SPM image (b) of the finally annealed ZnO film on SAP (0 0 0 1) substrate.

Off-axis φ-scans for {1 0 −1 1} reflections of ZnO have been widely used to examine the epitaxial relationship of the in-plane orientation of the ZnO films on single crystal. A ZnO crystal with *c*-axis orientation possesses sixfold symmetry. Thus, six poles should appear in the pole-figure if it has a homogeneous in-plane alignment. After setting $2\theta = 36.26^\circ$, which corresponds to the ZnO (1 0 −1 1) reflection, film was rotated from $\varphi = 0^\circ$ to 360° at tilted angles between $\psi = 0^\circ$ and 90°. As shown in Fig. 1(b), the six sharp spots of ZnO (1 0 −1 1) reflections corresponding to the *c*-axis orientation were observed every 60° with $\psi \cong 60^\circ$ for the ZnO film on SAP (0 0 0 1). The result of pole-figure analysis indicates that this ZnO film has an epitaxial relationship with SAP substrate.

UV transmission measurement was carried out for optical characterization of the epitaxial ZnO film. Fig. 2 shows the visible spectrum in the wavelength range from 200 nm to 1100 nm of epitaxially grown ZnO thin film on SAP (0 0 0 1) substrate after annealing at 750 °C. A high transmittance in the visible spectral range and clear absorption edge of the film were observed. The transmittance in the UV spectral region decreased abruptly near 3.28 eV, resulting from band-to-band transition. In this transition, UV absorption occurs due to the excitation of electrons from the filled valence band to the conduction band. Based on the optical absorption coefficient α of the film obtained from the transmittance using the relationship, $I = I_0 e^{-\alpha t}$, where I is the intensity of the transmitted light, I_0 is the intensity of the incident light, and t is the thickness of the film, the band gap energy of the film was calculated by plotting α^2 *vs.* $h\nu$ and extrapolating the linear position of the curves to $\alpha^2 = 0$, the band gap of the film is 3.28 eV, similar to the intrinsic band gap of ZnO.

PL spectroscopy provides additional insight into semiconductor crystal quality through emission from discrete states bordering and within the band gap, or states arising from structural defects. The PL spectra at room temperature of epitaxial ZnO thin film on SAP (0 0 0 1) substrate obtained by two-step pyrolysis and final annealing at 750 °C is shown in Fig. 3(a). The 325 nm line of a He–Cd laser was used to illuminate the ZnO film. As shown in Fig. 3(a), the dominant emission peak of the ZnO film was observed at 380 nm, which is tentatively attributed to the exciton transition bound to neutral donors. A deep-level emission band centered at 515 nm was also observed as indicated in Fig. 3(a). The origin of the deep-level emission is not yet clearly identified but it is presumably associated with structural defects or impurities [9]. The magnitude of the strain is too large and strain relief take place because of the large lattice mismatch (18.3%) between the ZnO film and the substrate used in this work. Strain relaxation can be accomplished by introducing misfit dislocations and three-dimensional grain growth [10]. This may cause the reduction in ZnO structural and optical quality, since broad deep-level emission band originates from structural defects, which from electron-hole recombination centres. ZnO/SAP is a pair with relatively high lattice misfit, which we conclude to be the main reason for deterred high-quality epitaxial growth.

Epitaxially and homogeneously grown films are suitable for high-quality devices, since the crystalline quality and surface morphology of the film is essential for fabricating devices with high performance. To evaluate the surface roughness and morphology of the film, SPM analysis was performed. Fig. 3(b) shows the SPM image (1 μm × 1 μm) of ZnO film after annealing at 750 °C. Three-dimensional growth was observed, although we can observe many regular and uniform grains in the SPM image of the film.

Although, in order to fabricate ZnO-based optoelectronic devices by using sol–gel process, further understanding of the relation between processing and structural dislocation due to large lattice mismatch still remain, structural, morphological and optical properties of heteroepitaxial ZnO/SAP structure showed the possibility of the method for cost-effective fabrication studies.

4. Conclusions

In this work, epitaxially grown ZnO thin film was prepared on SAP (0 0 0 1) substrate by a sol–gel process. From XRD θ–2θ scan, highly *c*-axis oriented ZnO was obtained and epitaxial relationship between ZnO film and SAP substrate was confirmed by XRD pole-figure analysis. A high transmittance above 90% in visible spectral range and clear absorption edge of the film were observed. From PL measurement, a strong NBE emission with a broad deep-level emission was observed at around 380 nm.

References

[1] A.B.M.A. Ashrafi, Y. Segawa, K. Shin, J. Yoo, T. Yao, Appl. Surf. Sci. 249 (2005) 139–144.

[2] K.K. Kim, J.H. Song, H.J. Jung, S.J. Park, J.H. Song, J.Y. Lee, J. Vac. Sci. Technol. A 18 (6) (2000) 2864–2868.

[3] S. Zhu, C.H. Su, S.L. Lehoczky, M.A. George, D.H. Lowndes, J. Mater. Res. 15 (5) (2000) 1125–1130.

[4] Y.S. Jeon, D.M. Kim, K.S. Hwang, Appl. Surf. Sci. 253 (2007) 7016–7018.

[5] K.S. Hwang, Y.S. Jeon, B.A. Kang, K. Nishio, T. Tsuchiya, J.H. An, B.H. Kim, J. Korean Phys. Soc. 46 (2) (2005) 521–526.

[6] B. Wessler, F.F. Lange, W. Mader, J. Mater. Res. 17 (7) (2002) 1644–1650.

[7] S. Hwangbo, Y.J. Lee, K.S. Hwang, Ceram. Int. 34 (2008) 1237–1239.

[8] R. Cebulla, R. Wendt, K. Ellmer, J. Appl. Phys. 83 (1988) 1087–1095.

[9] W.I. Park, S.J. An, G.C. Yi, H.M. Jang, J. Mater. Res. 16 (5) (2001) 1358–1362.

[10] B.P. Zhang, K. Wakatsuki, N.T. Binh, N. Usami, Y. Segawa, Thin Solid Films 499 (2004) 12–19.