O U R N A L O F

Ceramic Processing Research

Optoelectrical properties of ZnO thin films grown by pulsed laser deposition

Changsun Park and Kwangjoon Hong^{a,*}

Department of Metallurgical and Materials Engineering, Chosun University, Kwangju 501-759, Korea ^aDepartment of Physics, Chosun University, Kwangju 501-759, Korea

ZnO films on Al₂O₃ substrates were grown using a pulsed laser deposition method. Through photoluminescence (PL) and Xray diffraction (XRD) measurements, the optimum growth conditions for the ZnO growth were established. The results of the XRD measurements indicate that ZnO films were strongly oriented to the c-axis of the hexagonal structure and epitaxially crystallized under constraints created by the substrate. The full width half maximum for a theta curve of the (0002) peak was 0.201°. Also, from the PL measurements, the grown ZnO films were observed to give free exciton behaviour, which indicates a high quality of the epilayer. The Hall mobility and carrier density of the ZnO films at 293 K were estimated to be 299 cm²/ V s and 8.27×10¹⁶ cm⁻³, respectively. The absorption spectra revealed that the temperature dependence of the optical band gap on the ZnO films was $E_g(T)=3.4393$ eV–(5.30×10^{-4} eV/K)T²/(367+T).

Key words: ZnO thin films, Pulsed laser deposition, optimum growth conditions, optical band gap, Hall mobility, carrier density.

Introduction

A II-VI compound semiconductor with a wide direct band gap of 3.37 eV at room temperature [1], Zinc oxide (ZnO) is an attractive material because of its optoelectronic applications such as for light emitting diodes (LED), laser diodes (LD), surface acoustic waves (SAW), and surface elastic-wave filters [2-6]. In particular, ZnO has a higher exciton binding energy of about 60 meV at room temperature than do the materials ZnSe and GaN [1]. This gives an advantage to the blue and/or ultraviolet LED as a substitute for GaN. Therefore, growth of ZnO has been attempted by several methods such as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), metalorganic chemical vapor deposition (MOCVD), radio frequency magnetron sputtering, etc. [3, 7-10]. However, PLD is a powerful technique for the deposition of oxides [11, 12]. Recently, extensive and successful efforts have been made for thin film growth of ZnO using PLD since it is an attractive choice for the preparation of stoichiometric and high quality ZnO films for various applications. Furthermore, PLD also has several other advantages including its ability to create high-energy source particles, permitting high quality film growth at low substrate temperatures, a simple experimental setup, and operation in high ambient gas pressures [13]. In particular, low temperature deposition using the PLD growth method is capable of solving the VI-element vacancy problem [14, 15].

In the present study, the ZnO films were grown on sapphire (Al_2O_3) substrates by a PLD method. The grown ZnO was investigated for its structural and optical characteristics by means of X-ray diffraction (XRD), photoluminescence (PL), and absorption spectroscopy. This paper reports on the optimum growth conditions, structural characteristics, and band gap.

Experimental Procedures

Figure 1 shows a schematic diagram of the PLD system for ZnO film growth. Prior to PLD growth, the ZnO target disk (3 mm thick and 12 mm in diameter) fabricated by compressing ZnO powder was used as a source of the PLD. In order to grow ZnO films, an ArF pulsed excimer laser (Lambda Physik, LPX110i, $\lambda =$ 193 nm) was used as a photon source. In order to get a uniform film thickness, the rotating speed of the target was kept at 40 rpm during the deposition. Also, pure oxygen gas as a background gas was used to create the ambient pressure during ZnO film growth. The laser repetition rate was 10 Hz, and the power per pulse was 100 mJ. Therefore, the energy density on the target was estimated to be 2 J/cm². At this time, the gas pressure was 10 Pa. The target-substrate distance was set at 4 cm. The substrate used for ZnO films was (0001) Al₂O₃. The surface of the substrates was cleaned in acetone, methanol, and ethanol for 5 minutes, respectively, and etched in H₂SO₄:H₂PO₄=3:1 for 7 minutes at 150 °C. Then, it was rinsed in the deionized water. To obtain the optimum growth conditions, the grown ZnO films were analyzed by XRD and PL measurements. The PL measurement of the samples was performed at 10 K in a low temperature cryostat equipment (AP Inc. CSA

^{*}Corresponding author:

Tel:+82-62-230-6637

Fax: +82-62-234-4326

E-mail: kjhong@mail.chosun.ac.kr

Quartz Window

Laser Beam Rotator System

Pulsed Laser



Fig. 1. A schematic diagram of the PLD system for ZnO film growth.

Stainleess Steel

Vacuum System

202B, DE 202S) during the excitement of the He-Cd laser (Kimmon, 442 nm, 50 mW). The thickness of the ZnO films was measured by an α -step profilometer (Tenco, a-step 200). In addition, the electrical properties were achieved by Hall effect measurements using the van der Pauw method at various temperatures. To measure the energy band gap, the optical absorption experiment was performed on a UV-VIS-NIR spectrophotometer (Hitachi, U-3501) for a range from 360 nm to 370 nm at various temperatures from 10 K to 293 K.

Result and Discussion

Growth parameters and structural properties

ZnO films were grown by varying the substrate temperature from 380 to 420 °C. To find the optimum growth conditions, PL measurements on the grown films were performed at 10 K, and the XRD measurements were conducted at room temperature. Among the PL spectra obtained, the emissions caused by excitons were used to predict the crystal quality critera of the grown films because excitons could only be observed in the defective crystals at low temperature. Therefore, free exciton (E_x) and neutral donor bound exciton (D°, X) emissions were used for the optimum growth conditions. Also the self-activated (SA) emission was checked. Ordinarily, the exciton intensity has a tendency to increase, and the SA peak is inclined to decrease with the quality of a crystal at low temperature. In addition,

Table 1. Comparison of the PL intensity and the XRD curves as
a function of substrate temperature(arbitrary units)

Substrate	Intensity of PL at10K			XRD	
temperature	E_{x}	(D^{o}, X)	SA	Intensity (×10 ⁴)	FWHM
380 °C	0	63	10	0.85	0.219°
400 °C	48	108	18	1.34	0.201°
420 °C	0	77	28	1.10	0.208°

the intensity and the full width half maximum (FWHM) of the XRD curves were used for crystal quality evaluation of ZnO films. As shown in Table 1, the highest (D°, X) peak and a very weak SA peak were observed in the film which was grown while the substrate temperature was kept at 400 °C. Also, the E_x emission was observed only at a substrate temperature of 400 °C.

Temperature

controller

This observation indicates that the ZnO film grown at 400 °C has a very high quality because the emission peak of the free exciton can be observed only under the conditions of a long-range Coulomb coupling between an electron and a hole. Thus, to certify crystalline quality, the evaluation of ZnO films was enhanced by the XRD method. As shown in Table 1, the highest intensity and the narrowest FWHM of a XRD curve were observed in ZnO films grown at 400 °C. To grow the ZnO films, the optimum temperature of the substrate was found to be 400 °C. Table 2 presents the optimum growth conditions for high quality ZnO films using the PLD method. Therefore, ZnO films grown by the growth conditions in Table 2 were used to achieve a thickness of 2.9 µm and a growth rate of 1.45 µm/hr. Here, the growth rate of the film is comparatively high. The PLD growth method is known to deliver more energetic atomic species to the substrate, several tens or hundreds times higher than MBE. Figure 2 shows the

 Table 2. Optimum growth conditions of the PLD method for the high quality ZnO films

Optimum values	
400 °C	
40 rpm	
10 Hz	
100 mJ	
10 Pa	
4 cm	



Fig. 2. The surface morphology by SEM of a ZnO film grown under optimized conditions.

surface morphology by scanning electron microscopy (SEM) of a ZnO film grown under optimized conditions. As shown in Fig. 2, the morphology revealed a very smooth surface, and some contrast was observed about the presence of crystalline grains. Figure 3 presents the XRD spectrum of a ZnO film grown under optimized conditions.

These patterns correspond to the diffraction peaks of the ZnO (0002) and Al_2O_3 (0006). The intensity of the ZnO (0002) peak located at a two theta of 34.477° is very sharp and dominant. This indicates that the film is strongly oriented to the c-axis of the hexagonal structure and also crystallized under constraints created by the substrate. Therefore, this means that the ZnO film is epitaxially crystallized even though the lattice mismatch between ZnO and Al_2O_3 is very large. The FWHM for the (0002) peak is 0.201°. This value is better than that of 0.35° obtained from the PLD method by Ryu et al. [16], and similar to the value of 0.197° grown from MBE method by Wang et al. [17].

From the Hall effect measurements, the measured mobility and carrier density at 293 K were 299 cm²/V s and 8.27×10^{16} cm⁻³, respectively. The mobility tended to increase during a decrease to the temperature of 100



Fig. 3. A XRD spectrum of a ZnO film grown under optimized conditions.



Fig. 4. Optical absorption spectra obtained in the temperature range of 10 K to 293 K.

K, and thereafter, it decreased. At the apex of 100 K, it showed the largest value of 998 cm^2/V s. The ZnO film grown was confirmed to be n-type. The samples grown were always n-type owing presumably to slight stoichiometric deviations originating from an excess of oxygen vacancies.

Optical absorption measurements

Figure 4 shows the optical absorption spectra obtained in the temperature range of 10 K to 293 K. To identify the energy band gap for ZnO films, we carefully examined the relation between the optical absorption coefficient (α) and the incident photon energy (hv) from the optical absorption measurements in Fig. 4. The relation for a direct band gap between hv and α is given by:

$$(\alpha h\nu)^2 \sim (h\nu - E_g). \tag{1}$$

Figure 5 displays the band gap energy variation of ZnO film using Eq. (1) as a function of temperature. This figure does not follow the conventional linear relationship. Therefore, the temperature dependence of the optical energy band gap in our experiment is well fitted numerically by the following formula [18, 19]:

$$E_{g}(T) = E_{g}(0) - \alpha T^{2} / (T + \beta),$$
 (2)



Fig. 5. Optical energy band gap of ZnO films plotted as a function of temperature.

where α is a constant and β is approximately the Debye temperature. Also, $E_g(0)$ is the energy band gap at 0 K, which is estimated to be 3.4393 eV. When α and β are taken to be 5.30×10^{-4} eV/K and 367 K, respectively, the curve plotted by Eq. (2) closely fits the experimental values, as shown in Fig. 5. However, $E_g(0)$ and a were nearly consistent to the values obtained by Ray [20]. Also, the Debye temperature of ZnO was found to be 370 K [21] and in a reasonable agreement with our result.

Conclusions

ZnO films were grown on Al₂O₃ substrates using a PLD method and the optimum growth conditions were described. The results of the PL and the XRD measurements revealed that the grown ZnO films are highly crystalline and good quality. The results of the XRD measurements indicate that ZnO films are strongly oriented to the c-axis of the hexagonal structure and epitaxially crystallized under constraints created by the substrate. The FWHM the (0002) peak turned out to be 0.201°. This value corresponded to that of a film grown using an MBE method. The Hall mobility and the carrier density of the ZnO film at 293 K were estimated to be 299 cm²/V s and 8.27×10^{16} cm⁻³, respectively. Finally, the optical band gap obtained from the absorption measurements was well described by the Varshni's relation, Eg(T)=3.4393 eV-(5.30×10⁻⁴ eV/K)T²/(367+T).

Acknowledgement

This study was supported by research funds from Chosun University, 2006.

References

- 1. B. Lin, Z. Fu, and Y. Jia, Appl. Phys. Lett. 79 (2001) 943-947.
- K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. 79 (2001) 988-991.
- Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270-3275.
- D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, M.Y. Shen, and T. Goto, Appl. Phys. Lett. 73 (1998) 1038-1042.
- M.-S. Wu, A. Azuma, T. Shiosaki, and A. Kawabata, J. Appl. Phys. 62 (1987) 2482-2485.
- 6. F.S. Hickernell, J. Appl. Phys. 41 (1973) 1061-1066.
- Y. Chen, D.M. Bagnall, Z. Zhu, T. Sekiuchi, K. Park, K. Hiraga, T. Yao, S. Koyama, M.Y. Shen, and T. Goto, J. Crystal Growth 181 (1997) 165-169.
- 8. F.T.J. Smith, Appl. Phys. Lett. 43 (1983) 1108-1112.
- K.B. Sundaram and A. Khan, Thin Solid Films 295 (1997) 87-92.
- Y. Nakata, T. Okada, and M. Maeda, Appl. Surf. Sci. 197/ 198 (2002) 368-372.
- Y. Nakata, G. Soumagne, T. Okada, and M. Maeda, Appl. Surf. Sci. 129 (1998) 650-655.
- C.V. Ramana, R.J. Smith, O.M. Hussain, and C.M. Julien, Mater. Sci. Eng. B 111 (2004) 218-222.
- L.N. Dinh, M.A. Schildbach, M. Balooch, and W. McLean II, J. Appl. Phys. 86 (1999) 1149-1154.
- M. Chu, S. Terterian, D. Ting, C.C. Wang, H.K. Gurgenian, and S. Mesropian, Appl. Phys. Lett. 79 (2001) 2728-2731.
- S.D. Setzler, M. Moldovan, Z. Yu, T.H. Myers, N.C. Giles, and L.E. Halliburton, Appl. Phys. Lett. 70 (1997) 2274-2277.
- Y.R. Ryu, S. Zhu, J.M. Wrobel, H.M. Jeong, P.F. Miceli, and H.W. White, J. Crystal Growth 216 (2000) 326-329.
- X. Wang, S. Yang, J. Wang, M. Li, X. Jiang, G. Du, X. Liu, and R.P.H. Chang, J. Crystal Growth 226 (2001) 123-128.
- Y. P. Varshni, Physica 34 (1967) 149-153.
 K.J. Hong, T.S. Jeong, C.J. Yoon, and Y.J. Shin, J. Crystal Growth 218 (2000) 19-25.
- 20. B. Ray, II-VI Compounds, (Pergamon, Oxford, 1969) 54-59.
- E. Mollwo, in Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, edited by O. Madelung (Springer, Berlin, 1982), Vol. 17h, 35-42.