Structural, Electrical and Optical Properties of ZnO Thin Films Grown at Various Plume-Substrate Angles by Pulsed Laser Deposition

Jae-Won Kim*, Hong-Seong Kang* and Sang-Yeol Lee†

Abstract - ZnO thin films were grown at different plume-substrate (P-S) angles of 90° (on-axis PLD), 45° and 0° (off-axis PLD) using pulsed laser deposition. The x-ray diffraction pattern exhibiting a dominant (002) and a minor (101) peak of ZnO indicates all films were strongly c-axis oriented. By observing of (002) peak, the FWHMs of ZnO (002) peaks decreased and c-axis lattice constant approached the value of bulk ZnO as P-S angle decreased. Whereas the carrier concentration of ZnO thin film deposited at P-S angle of 90° was ~10^{19}/cm^3, the Hall measurement of ZnO thin films deposited at P-S angles of 0° and 45° was impossible due to the decrease of the carrier concentration by the improvement of stoichiometry and crystalline quality. By decreasing P-S angle, the grain size of the films and the UV intensity investigated by photoluminescence (PL) increased and UV peak position showed red shift. The improvement of properties in ZnO thin films deposited by off-axis technique was due to the decrease of repulsive force between a substrate and the particle in plume and the relaxation of supersaturation.

Keywords: ZnO thin film; Plume-substrate angle; Off-axis; Pulsed laser deposition

1. Introduction

The recent availability of high crystalline quality ZnO thin film and its attractive properties, such as wide band gap energy at room temperature(3.37 eV), large exciton binding energy(60 meV) and optical transparency present new possibilities for applications to short wavelength light emitting devices [1]-[4]. Among various growth techniques of ZnO thin film, pulsed laser deposition(PLD) has advantages of being able to not only employ a relatively high oxygen pressure but also achieve high-quality crystalline films with relatively high deposition rate at low temperatures due to the high energy (~100 eV) of the ablated particles in the laser produced plume [5]. A study on off-axis PLD where a substrate is positioned parallel to the laser-produced plume was reported by Holzapfel *et al.* in 1992 [6]. The number of density of micron-sized particles of YBCO films decreased to zero with only a factor of 3 reduction in deposition rate and outgrowth density associated with nonstoichiometric phases of YBCO films diminished in the study.

In this study, ZnO thin films were grown at various plume-substrate (P-S) angles without changing other experimental parameters, such as energy density of laser, ambient gas pressure and the distance between a target and a substrate. The properties of ZnO thin films were systematically investigated as a function of P-S angle.

† Corresponding Author: Dept. of Electrical and Electronic Engineering, Yonsei Univerity, Korea.(sylee@yonsei.ac.kr)
* Dept. of Electrical and Electronic Engineering, Yonsei Univerity, Korea.
Received February 2, 2005; Accepted May 17, 2005

2. Experimental

ZnO thin films were deposited on (001) sapphire substrates at various P-S angles by a pulsed laser deposition. P-S angle was defined as angle between the substrate surface and the plume propagation direction. Three different P-S angles were used as 0°, 45° and 90°. In general PLD system (on-axis PLD system), P-S angle is 90°. The schematic of PLD system and P-S angles were shown in Fig. 1. Pulsed Nd:YAG laser was operated at a wavelength of 355 nm. The energy density and repetition rate of a laser were 2.5 J/cm^2 and 5 Hz. The focused laser beam illuminated on a rotating ZnO target at 33.7° incident angle. The deposition chamber was initially evacuated to the pressure in the range from 10^{-6} to 10^{-7} Torr by turbomolecular pump, and finally filled with 99.99 % pure oxygen of 350 mTorr. The target was a 99.999 % pure ceramic ZnO target, and the distance between a target and the center of a substrate was 50 mm. The substrate temperature was at 400℃ and the thickness of ZnO thin films was about 7,300 Å. The crystal quality was investigated by XRD with a Ni-filtered CuKα (λ=1.5418 × 10^{-10} m) source. The surface morphology was observed by atomic force microscopy (AFM). The optical properties of ZnO thin films were characterized by photoluminescence (PL) with a HeCd laser as a light source using the

excitation wavelength of 325 nm and the power of 20 mW. The electrical properties were measured by Van der Pauw Hall measurements. All measurements were performed at room temperature.

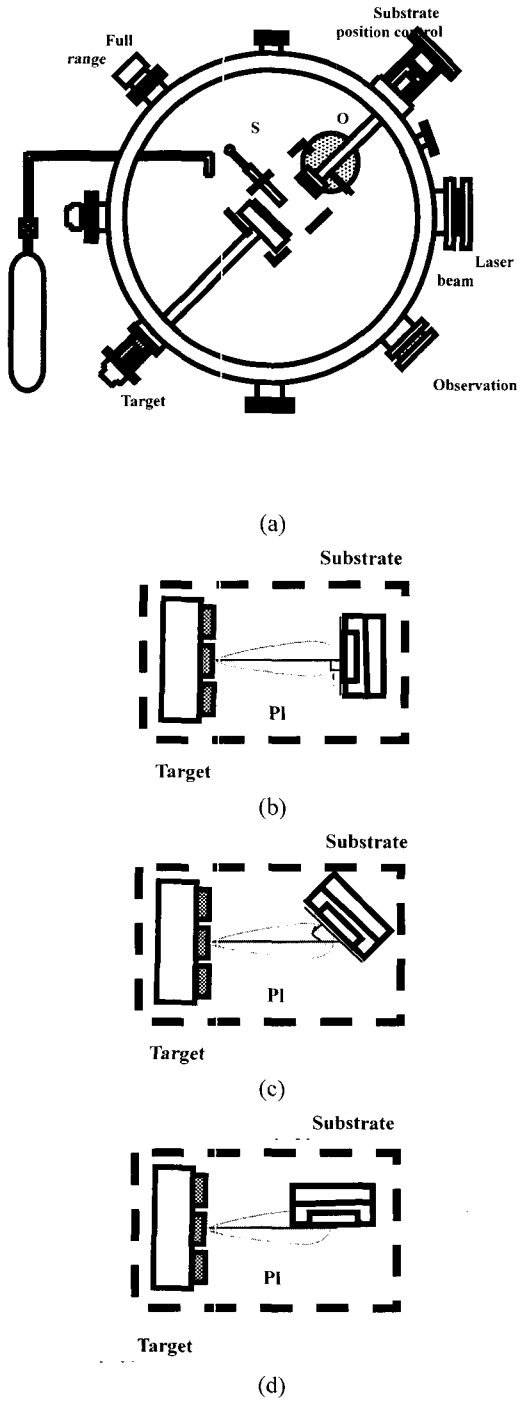


Fig. 1 Schematic of (a) PLD system, (b) P-S angle of 90°, (c) P-S angle of 45°, (d) P-S angle of 0°.

3. Results and discussion

The deposition time and growth rate of ZnO thin films are summarized at Table 1. The growth rate and film thickness depending on P-S angle was investigated by cross sectional scanning electron microscopy (SEM) images of ZnO thin films. As P-S angle decreased, the growth rate per laser shot decreased. This indicates that the amount of ablated species arriving on a substrate per laser shot decreases by tilting angle between the substrate surface and the plume propagation direction in the PLD system.

Table 1 The deposition time and growth rate of ZnO thin films deposited at various P-S angles.

P-S angle (°)	Deposition Time (sec)	Growth Rate per Laser Shot (Å /shot)
90	600	2.43
45	992	1.47
0	1,430	1.02

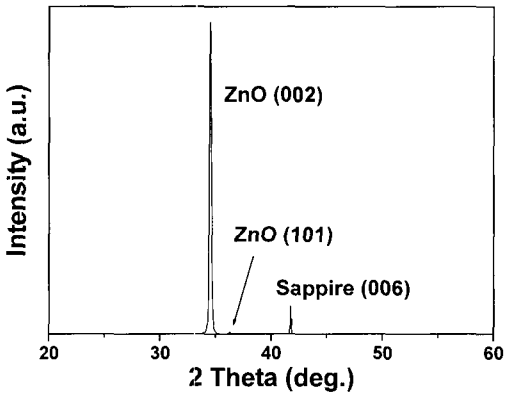


Fig. 2 XRD spectrum of ZnO film deposited at the P-S angle of 45°

Fig. 2 shows XRD spectrum of ZnO film deposited at P-S angle of 45°. All films were found to be well c-axis oriented exhibiting a dominant (002) and a minor (101) peaks of ZnO. Fig. 3 shows (002) peaks of ZnO thin films. As P-S angle decreased, the full widths at half maximum (FWHMs) of (002) ZnO peaks decreased and the position of (002) peak was shifted to lower angle. The FWHMs of (002) ZnO peaks were 0.213° for 90°, 0.208° for 45° and 0.198° for 0°. Lattice constants calculated by the (002) peak positions were 5.1934 Å, 5.1978 Å and 5.2007 Å, respectively and approached to the value of bulk ZnO (5.2069 Å) as P-S angle decreased [7]. The change of c-axis constant depending on P-S angle was summarized in table 2. The increase of c-axis constant toward that of bulk ZnO indicates that all ZnO films are under tensile strain. This tensile strain has been relaxed by tilting P-S angle from 90° to 0°. Generally, ZnO thin films grown at Al_2O_3 substrates are under compressive strain due to 18% lattice mismatch with substrate [8]. However, the mechanism in which ZnO films are under tensile strain was reported by

H.S. Kang and M. Kawasaki *et al.*[1],[9]. All diffraction peaks in Fig. 3 are asymmetric, where the peaks are broadened at the side of the high diffraction angle, corresponding to a smaller inter-plane spacing along c-axis. It also indicates that all films are under tensile strain indirectly [10].

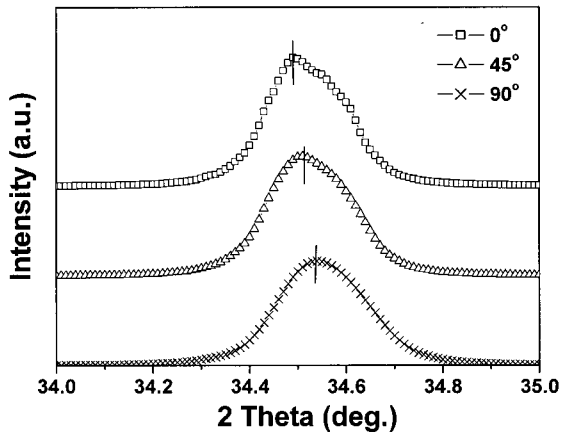


Fig. 3 XRD spectra of ZnO films deposited at different P-S angles: (002) peak

Fig. 4 shows 2 X 2 μm^2 AFM images of ZnO thin films deposited at various P-S angles. The grain size was observed to be increased as P-S angle decreased. It is consistent with the change of XRD FWHM of (002) peak. Generally, the increase of grain size in film means the decrease of FWHM of XRD spectrum and the improvement of crystalline quality.

Ideally, defect-free ZnO film is an insulator. However, as-grown films show n-type semiconducting properties because of many defects, such as the oxygen vacancies and Zn interstitials. The carrier concentration of ZnO thin film deposited at P-S angle of 90° was ~$10^{19}/cm^3$. On the other hand, the Hall measurement of ZnO thin films deposited at P-S angles of 0° and 45° was impossible due to the decrease of the carrier concentration by the improvement of stoichiometry and crystalline quality. This result is consistent with the decrease of XRD FWHM of ZnO (002) peaks, the increase of grain size in Fig. 4 and PL results in Fig. 5.

Fig. 5 shows PL spectra of ZnO thin films deposited at different P-S angles. UV emissions at ~ 380 nm (3.26 eV) were observed for all films, which is in good agreement with typically reported free exciton peak position [4],[11]. Intensity of UV emission which strongly depends on the stoichiometry of the films [12]-[16] increased remarkably and the position of UV peaks showed red shift from 380 nm to 385 nm as the P-S angle decreased. The increase of UV intensity means that the stoichiometry of ZnO thin film improves [12]-[16]. From shift of XRD peak position in Fig. 3 and the result of Hall measurement, it should be considered that the variation of interatomic spacing and relaxation of Burstein-Moss shift by decrease of carrier concentration as decrease of P-S angle result in the red shift of UV emission peak of ZnO thin film [17]-[19].

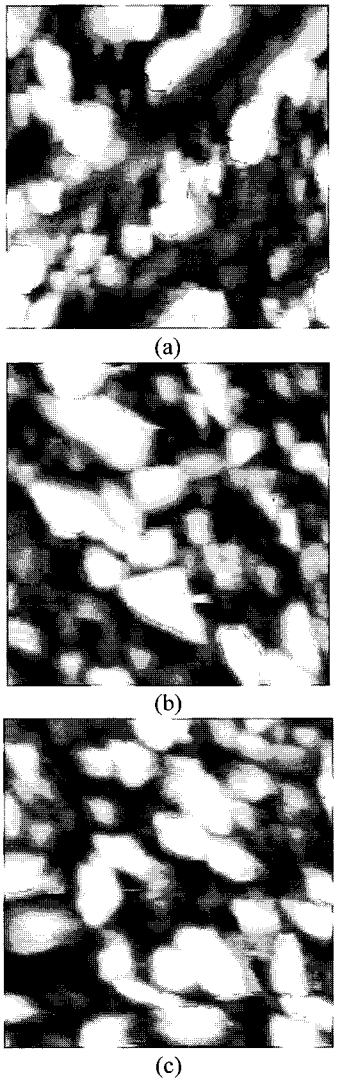


Fig. 4 AFM images of ZnO thin films of 2 X 2 μm^2 deposited at P-S angles of (a) 90°, (b) 45° and (c) 0°

(1) The target-substrate distance or (2) the substrate-plume distance or (3) the decrease of repulsive force by collision between a substrate and particle in plume arriving on a substrate or (4) the reduction of flux of ablated species arriving on a substrate could be reasons for the improvement of properties in the ZnO thin films deposited by off-axis technique. However, all thin films in this study were deposited at the center of substrate and the same target-substrate distance. Substrate-plume distance is also same as on-axis case due to tilting the substrate at the center of the plume. Since XRD, AFM and PL were measured at the center of all thin film, substrate-plume

distance and target-substrate distance could not lead the change of the properties of the films grown by off-axis technique. Therefore, the possible explanations for the improvement of properties in ZnO thin films deposited by off-axis technique could be (3) and (4).

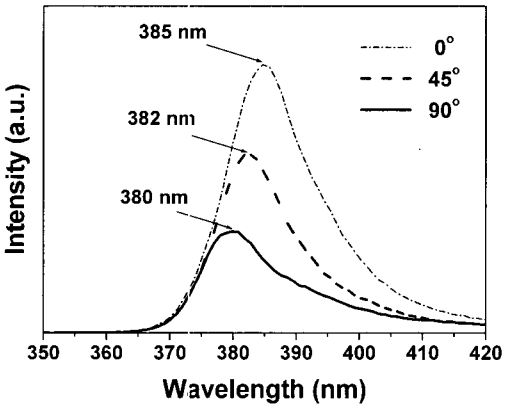


Fig. 5 PL spectra of ZnO thin films deposited at different P-S angles.

Table 2 Variations of c-axis lattice constant and UV peak position of ZnO thin films depending on P-S angle.

P-S angle (°)	c (Å)	UV peak position (nm)
90	5.1934	380
45	5.1978	382
0	5.2007	385
Bulk ZnO	5.2069	-

In case of on-axis technique, the repulsive force by collision between a substrate and particle in plume arriving on a substrate is strong because the particle in plume collides head-on with the substrate as shown in Fig. 1 (b). However, the repulsive force in off-axis technique decreases because a substrate and the particle in plume arriving on a substrate have a broadside collision as shown in Fig.1 (c), (d). The decrease of repulsive force in off-axis technique caused increase of adatom mobility of the particle on a substrate and it led improvement of the properties in the ZnO film.

It is well known that films are often grown at high supersaturation, that is, the flux of impinging particle is so high, and the substrate temperature so low, that incoming particles cannot sample the whole phase-space when they lend on the surface [20],[21]. The amount of ablated species arriving on a substrate per laser shot decreased as P-S angle decreased as shown in Table 1. The decrease of the amount of ablated species arriving on a substrate per laser shot in films grown by off-axis technique relaxes the supersaturation effect and results in the improvement of the film properties.

5. Conclusion

Off-axis technique tilting substrate surface to the plume propagation direction in PLD system was suggested to deposit ZnO thin films. As P-S angle decreased, XRD FWHMs of ZnO (002) peaks decreased and lattice constant of ZnO films was shifted to the value of bulk ZnO. The grain size and UV luminescent intensity increased as P-S angle decreased. The Hall measurement of ZnO thin film deposited at P-S angles of 0° and 45° was impossible due to the decrease of the carrier concentration by the improvement of stoichiometry and crystalline quality. It is concluded that the decrease of repulsive force between a substrate and the particle in plume and the relaxation of supersaturation by decreasing the amount of laser-ablated species arriving on the surface of a substrate or film per laser shot in off-axis technique lead to improve properties of ZnO thin films.

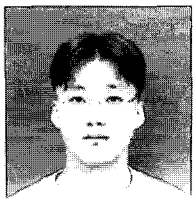
Acknowledgements

This work was supported by government (R01-2004-000-10195-0(2004)) from the basic research program of KOSEF (Korea Science and Engineering Foundation).

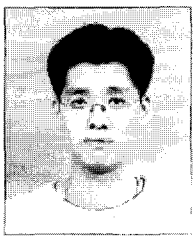
References

[1] Hong Seong Kang, Jeong Seok Kang, Jae Won Kim, Sang Yeol Lee, J. Appl. Phys 95 (2004) 1246.
[2] Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.
[3] S. H. Bae, S. Y. Lee, H. Y. Kim, S. Im, Optical Materials 17 (2001) 327.
[4] E. S. Shim, H. S. Kang, J. S. Kang, J. H. Kim, S. Y. Lee, Applied Surface Science 186 (2002) 474.
[5] Jeong Seok Kang, Hong Seong Kang, Seong Sik Pang, Eun Sub Shim, and Sang Yeol Lee, Thin Solid Films, 443, (2003) 5.
[6] Douglas B. Chrisey, Graham K. Hubler, Pulsed Laser Deposition of Thin Films, Willey, New York, (1994).
[7] S. King, J. G. E. Gardeniers, I. W. Boyd, Applied Surface Science 96-98 (1996) 811.
[8] J. M. Myoung, W. H. Yoon, D. H. Lee, I. Yun, S. H. Bae, S. Y. Lee, Jpn. J. Appl. Phys. 41 (2002) 28.
[9] M. Kawasaki, A. Ohtomo, I. Ohkubo, H. Koinuma, Z. K. Tang, P. Yu, G. K. L Wong, B. P. Ahang, Y. Segawa, Materials Science and Engineering B56 (1998) 239.
[10] Y. Chen, D. Bagnall, T. Yao, Materials Science and Engineering B75 (2000) 190.
[11] H. S. Kang, J. S. Kang, S. S. Pang, E. S. Shim, S. Y.

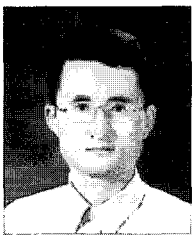
Lee. Materials Science and Engineering B102 (2003) 313.
[12] Sang Hyuck Bae, Sang Yeol lee, Beom Jun Jin, Seongil Im, Applied Surface Science 169-170 (2001) 525.
[13] K. I. Ogata, T. Kawanishi, K. Maejima, K. Sakurai, S. Fujita, S. Fujita, Jpn. J. Appl. Phys. 40 (2001) 657.
[14] Y. R. Ryu, S. Zhu, D.C. Look, J. M. Wrobel, H.M. Jeong, H.W. White, J. Cryst. Growth 216 (2000) 330.
[15] K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, Appl. Phys. Lett. 68 (1996) 403.
[16] S. Choopun, R. D. Vispute, W. Noch, A. Balsamo, R. P. Sharma, T. Venkatesan, A. Iliadis, D. C. Look, Appl. Phys. Lett. 75 (1999) 3947.
[17] P. Bhattacharya, Semiconductor Optoelectronic Devices, Prentice Hall, Upper Saddle River, New Jersey, 1997, p. 69, 70, 131.
[18] T. Makino, Y. Segawa, S. Yoshida, A. Tsukazaki, A.Ohtomo, M. Kawasaki, Appl. Phys. Lett. 85 (2004) 759.
[19] Tomoaki Terasako, Sho Shirakata, Tetsuya Kariya, Thin Solid Films 420-421 (2002) 13.
[20] Janos H. Fendler and Imre Dékány, Nanoparticles in Solids and Solutions, NATO ASI Series, (1996).
[21] Deuk-Kyu Hwang, Kyu-Hyun Bang, Min-Chang Jeong, Jae-Min Myoung, J. Cryst. Growth 254, (2003), 449.



Jae-Won Kim
He received B.S. and M.S. degree in Electrical and Electronic Engineering from Yonsei university, Korea.



Hong-Seong Kang
He received B.S. degree in electrical Engineering from Myongji university and M.S. degree in Electrical and Electronic Engineering from Yonsei university, Korea. He is currently Ph.D. candidate in Electrical and Electronic Engineering in Yonsei university, Korea.



Sang-Yeol Lee
He received BS degree in Electrical Engineering from Yonsei university, Korea, and M.S. amd Ph.D. in Electrical Engineering from State university of New York at Buffalo, N.Y, USA. He is a Professor in Department of Electrical and Electronic Engineering, Yonsei university, Korea. His research interests are semiconductor processing, optoelectronic device, display device, memory device, and nanoelectronics.