

Effect of annealing on the photoluminescence characteristics of ZnO thin films grown on the sapphire substrate by atomic layer epitaxy

Jongmin Lim, Kyoungchul Shin, Hyoun Woo Kim, Chongmu Lee*

Department of Materials Science and Engineering, Inha University, Incheon 402-751, South Korea

Received 8 September 2003; accepted 10 December 2003

Abstract

High-quality ZnO thin films have been grown on sapphire substrates by the atomic layer epitaxy (ALE) technique using diethylzinc (DEZn) and H₂O as reactant gases at substrate temperatures of 170 and 400 °C. In order to investigate the effect of annealing treatment on the optical properties of ZnO films, the films have been annealed at various annealing temperatures after deposition. After the annealing treatment the optical properties of ZnO thin films were characterized by photoluminescence (PL). A strong free exciton emission with a weak defect-band emission in the visible region was observed at room temperature (RT). Full width at half-maximum (FWHM) measurement of the free exciton emission of 67.54 meV have been made at room temperature. Based on the temperature dependence of the PL spectra in the temperature range from 10 K to room temperature it has been shown that the crystalline quality of the films increases as the annealing temperature increases. Also it shows that the best result is obtained when the sample is deposited at 170 °C and annealed at 1000 °C.

© 2004 Elsevier B.V. All rights reserved.

Keywords: ZnO; Atomic layer epitaxy; Photoluminescence; Annealing

1. Introduction

ZnO is a semiconductor with many attractive features. It has rapidly emerged as a promising optoelectronic material due to its large band gap of 3.37 eV at room temperature (RT), low power threshold for optical pumping at room temperature, and highly efficient UV emission resulted from a large exciton binding energy of 60 meV. Moreover, ZnO is thermally and chemically stable in air. Because of versatile physical properties ZnO has various applications such as transparent conductive contacts [1], thin film gas sensors [2,3], varistors [4], surface electroacoustic wave devices [5], UV laser [6,7] and others [8]. ZnO has exerted strong fascination and has grown interest, especially since Service [9] reported its potential application as an UV laser diode. Recently optically pumped stimulated emission and lasing of ZnO have been demonstrated, even at room temperature [10–12].

ZnO epitaxial films have mainly been made using sapphire substrates [13,14]. This is because Sapphire has the

same crystal structure as ZnO and relatively little lattice mismatch with ZnO. In order to increase the uniformity of the film thickness and the grain size of ZnO films, we have used the atomic layer epitaxy (ALE) technique, which has a basic advantage of excellent surface control during successful growth [15]. However, the ALE technique was rarely applied to epitaxial growth of ZnO and successful growth of high-quality epitaxial ZnO films by ALE has not been reported [16–21] yet as far as the authors know. The properties of ZnO thin films are much influenced by not only the growth methods (such as sputtering, spray pyrolysis, MOCVD, and MBE) but also the growth and postannealing process parameters. Therefore, it is important to study the influence of annealing on the properties of ZnO films. Here we report the improved crystallinity of ZnO after annealing treatment investigated with the help of the photoluminescence (PL) analysis.

Atomic layer controlled growth, or atomic layer epitaxy is a chemical vapor deposition (CVD) technique where the precursor species are introduced alternately. Contrary to the conventional CVD, the reaction proceeds only at the surface via chemisorbed species, so that the film growth is self limiting. This technique allows deposition over large area substrates with excellent thickness uniformity. Additionally,

* Corresponding author. Tel.: +82-32-860-7536;

fax: +82-32-862-5546.

E-mail address: cmlee@inha.ac.kr (C. Lee).

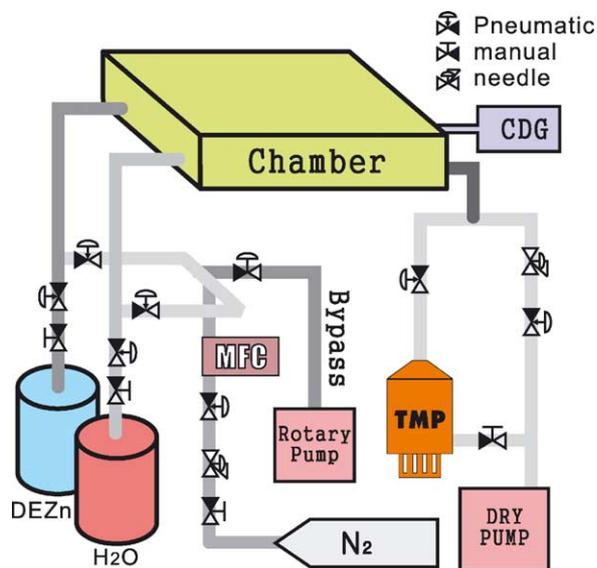


Fig. 1. A schematic diagram of the ALE system.

ALE is usually beneficial to growing films at lower temperatures than other classical methods including CVD.

2. Experimental

ZnO films were deposited on sapphire substrates using the ALE technique. Diethylzinc (DEZn) and H₂O were kept in bubblers at 10 °C. These source gases were alternately fed into the chamber through separate inlet lines and nozzles. The opening and closing sequences of the air valves were controlled by a computer. The typical pulse lengths were 1 s for DEZn, 5 s for the H₂O, and 10 s for purge between the reactants. The substrate temperatures were varied between 170 and 400 °C. The pressure in the chamber during the deposition was varied between 0.3 and 0.5 Torr. The schematic diagram of the deposition system is shown in Fig. 1. The optical properties of ZnO thin films were characterized by photoluminescence with He–Xe laser as a light source using an excitation wavelength of 325 nm and a power of 200 mW. In order to investigate the effect of annealing treatment, films have been annealed at various annealing temperatures from 600 to 1000 °C in an oxygen atmosphere for 1 h after deposition using a rapid thermal annealing (RTA) technique.

3. Results and discussion

Room temperature PL spectra of annealed ZnO thin films at temperatures of 600–1000 °C are shown in Fig. 2. As the annealing temperature increased, the intensities of both the UV (at about 3.26 eV) peak and that of visible (2.34–2.53 eV: green luminescence) peak increased.

Various mechanisms have been proposed for the green luminescence of ZnO. Vanheusden et al. [22] found that singly

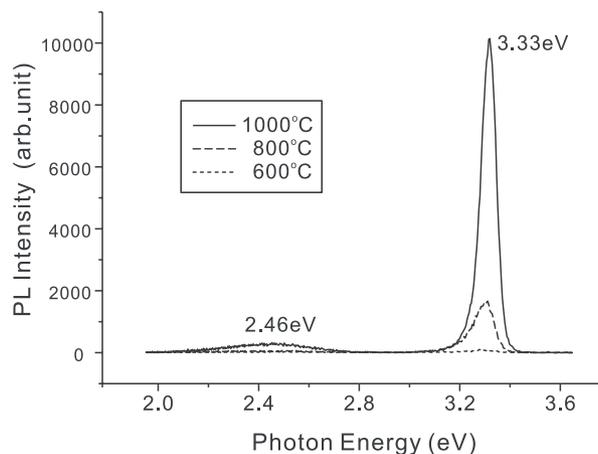


Fig. 2. Room temperature PL spectra of ZnO samples annealed at 1000, 800, and 600 °C for 1 h in an oxygen atmosphere after deposition at a substrate temperature of 170 °C.

ionized oxygen vacancies (V_O^*) are responsible for the green luminescence in the ZnO. Oxygen vacancies occur in three different charge states: the neutral oxygen vacancy (V_O^*), the singly ionized oxygen vacancy (V_O^+), and the doubly ionized oxygen vacancy (V_O^{2+}) and only the singly ionized oxygen vacancy (V_O^+) can act as the so-called luminescent centers [14]. The visible luminescence (2.34–2.53 eV) of the ZnO thin film was enhanced as the annealing temperature increased as shown in Fig. 2. It can be explained as follows: The more the ZnO thin films are heated to higher annealing temperatures, the more oxygen they lose, so that visible luminescence is enhanced. From these investigations, it may be concluded that increase of the visible luminescence of the ZnO film is strongly related to increase of the oxygen vacancy concentration by high annealing temperature process.

The sharp UV emission peak around the wavelength of 3.26–3.35 eV presumably results from excitons [23,24], which suggests that high-quality ZnO can be obtained at the deposition temperature of 170 °C and an annealing temperature of 1000 °C. Due to the large exciton binding energy of ZnO (about 60 meV), excitons have been observed at room temperature. It has also been reported that thermal energy at room temperature may be enough to release bound excitons because the binding energy of bound excitons is only a few milli-electron-volts [25]. To confirm that the UV band was due to the transitions of free excitons, temperature-dependent PL spectra were measured for a sample in the temperature range from 10 to 200 K as shown in Fig. 3. Temperature variation of a representative ZnO film is shown in Fig. 3. From the temperature variation of the PL measurement we can see that at a temperature as low as 10 K the intensity of the UV peak is very large compared with the peaks obtained at 20, 50, 100, and 200 K. Tang et al. [6] reported that UV PL is related to the microcrystalline structure. In the PL spectra (Fig. 3) we can see a strong peak of UV emission without any deep level peak at a temperature of about 10 K, which is commonly found

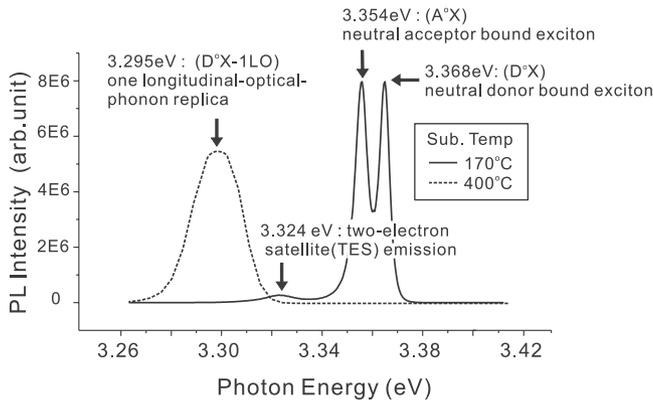


Fig. 3. PL spectra at 10K for representative ZnO films deposited at substrate temperatures of 170 and 400 °C and then annealed at 1000 °C for 1 h in an oxygen atmosphere.

at room temperature. The disappearance of the green band (deep level) in Fig. 3 demonstrates that the oxygen vacancy concentration is reduced at low temperature measurements.

In another set of experiments the ZnO films were deposited by ALE at a substrate temperature of 400 °C, and subsequently annealed by RTA at 700, 800, and 900 °C in a nitrogen atmosphere for 3 min. During the RTA process the ramping rate of temperature was kept constant at 8 °C/s. The PL at room temperature of this film shows a peak at 3720 Å due to UV emission. All the RTA-treated samples show a sharp UV emission peak. The intensity of the PL peak at UV emission increases with the annealing temperature as shown in Fig. 4, yet the intensity of the near-band-edge emission decreases probably due to defect formation above 900 °C. Nevertheless, the deep level emission is not observed.

One way to evaluate the concentration of structural defects in ZnO is to compare the relative PL intensity ratio of the UV-near-edge emission to the deep level green emission [26,27]. The PL spectra of our samples show relatively

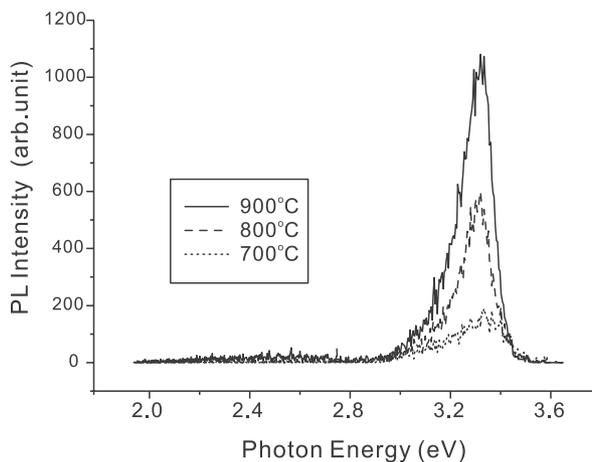


Fig. 4. Room temperature PL spectra of samples annealed by rapid thermal annealing process at 700, 800, and 900 °C for 3 min in a nitrogen atmosphere after deposition at the substrate temperature of 400 °C.

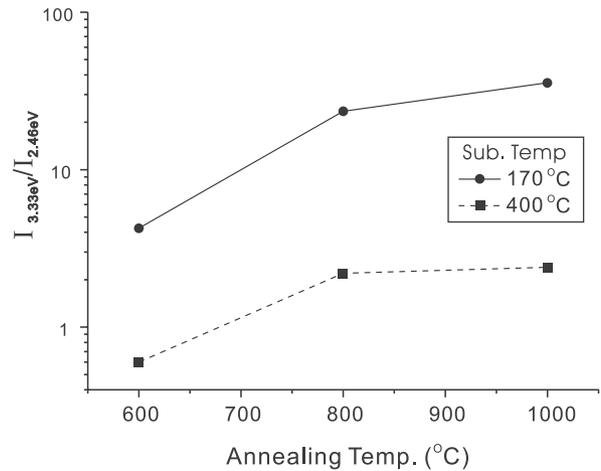


Fig. 5. The PL intensity ratio (R) of the UV-near-edge emission to the deep level green emission at different annealing temperatures.

weak deep level emission, indicating that the concentration of the defects responsible for the deep level is negligible. To evaluate the quality of the ZnO films, R defined as the ratio of the intensity of the ultraviolet near-band-edge emission to that of the deep level emission ($I_{3.33\text{ eV}}/I_{2.46\text{ eV}}$) was used. The bigger the ratio R , the higher the quality of the ZnO film [28]. Fig. 5 shows R values for different films deposited at 170 and 400 °C and annealed at different temperatures. It is evident from this figure that the annealing treatment after the ALE process enhances the ZnO film quality significantly.

4. Conclusion

In this paper, we have presented effects of annealing on the photoluminescence properties of ZnO films. The experimental results show that the crystal quality of ZnO films can be substantially improved by annealing them at 1000 °C for 1 hr in an oxygen atmosphere using the RTA technique. From the strong excitonic emission of the ZnO prepared by the ALE technique, it is evident that high-quality epitaxial ZnO thin films can be obtained by this technique, which can be used for highly efficient optoelectronic devices.

Acknowledgements

This work was supported by Korea Energy Management Corporation through 2002 Energy Science and Technology Promotion Program.

References

[1] K.L. Chopra, S. Major, D.K. Pandya, Thin Solid Films 102 (1983) 1.
 [2] N.J. Dayan, S.R. Sainkar, R.N. Karekar, R.C. Aiyyer, Thin Solid Films 325 (1998) 254.

- [3] P. Mitra, A.P. Chatterjee, H.S. Maiti, *J. Mater. Sci.* 9 (1998) 441.
- [4] C.S. Chen, C.T. Kuo, T.B. Wu, I.N. Lin, *Jpn. J. Appl. Phys. Part 1* 36 (1997) 1169 (Regular Papers Short Notes and Review Papers).
- [5] C.R. Gorla, N.W. Emanetoglu, S. Liang, W.E. Mayo, Y. Lu, M. Wraback, H. Shen, *J. Appl. Phys.* 85 (1999) 2595.
- [6] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Otono, H. Koinuma, Y. Segawa, *Appl. Phys. Lett.* 72 (1998) 3270.
- [7] D.C. Reynolds, D.C. Look, B. Jogai, *Solid State Commun.* 99 (1996) 873.
- [8] H.E. Brown, *ZnO Properties and Applications*, International Lead Zinc Research Organization, New York, 1976.
- [9] R.F. Service, *Science* 276 (1997) 895.
- [10] P. Yu, Z.K. Tang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, *J. Cryst. Growth* 184–185 (1998) 601.
- [11] Y.F. Chen, D.M. Bagnall, Z.Q. Zhu, T. Sekiuchi, K. Park, K. Hiraga, T. Yao, S. Koyama, M.Y. Chen, T. Goto, *J. Cryst. Growth* 181 (1997) 165.
- [12] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [13] C. Boemare, T. Monteiro, M.J. Soares, J.G. Guiherme, E. Alves, *Phys. B* 308–310 (2001) 985.
- [14] P. Fons, K. Iwata, S. Niki, A. Yamada, K. Matsuda, *J. Cryst. Growth* 201–202 (1999) 627.
- [15] T. Suntola, *Mater. Sci. Rep.* 4 (1989) 261.
- [16] H. Sato, T. Minami, S. Takata, T. Miyata, M. Ishii, *Thin Solid Films* 236 (1993) 14.
- [17] V. Lujala, J. Skarp, M. Tammenmaa, T. Suntola, *Appl. Surf. Sci.* 82–83 (1994) 34.
- [18] K. Saito, Y. Watanabe, K. Takahashi, T. Matsuzawa, B. Sang, M. Kongai, *Sol. Energy Mater. Sol. Cells* 49 (1997) 187.
- [19] A.W. Ott, R.P.H. Chang, *Mater. Chem. Phys.* 58 (1999) 132.
- [20] E.B. Yous, J. Fouache, D. Lincot, *Appl. Surf. Sci.* 153 (2000) 223.
- [21] Y. Yamato, K. Saito, K. Takahashi, M. Konagai, *Sol. Energy Mater. Sol. Cells* 65 (2001) 125.
- [22] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, *J. Appl. Phys.* 79 (10) (1996) 7990.
- [23] M.H. Huang, Y.Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [24] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, M.Y. Shen, T. Goto, *Appl. Phys. Lett.* 75 (1998) 1038.
- [25] P. Yu, Z.K. Tang, G.K.L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, *Solid State Commun.* 103 (1997) 459.
- [26] S. Bethe, H. Pan, B.W. Wesseis, *Appl. Phys. Lett.* 52 (2) (1988) 140.
- [27] G. Du, J. Wang, X. Wang, X. Jiang, S. Yang, Y. Ma, W. Yan, D. Gao, X. Liu, H. Cao, J. Xu, R.P.H. Chang, *Vacuum* 69 (2003) 476.
- [28] L. Martinu, D. Poitras, *J. Vac. Sci. Technol. A* 18 (2000) 2619.