Journal of Electroceramics, 13, 183–187, 2004
© 2004 Kluwer Academic Publishers. Manufactured in The Netherlands.

Photoluminescence of ZnO:Ga Thin Films Fabricated by Pulsed Laser Deposition Technique

Z.F. LIU,[1,4] F.K. SHAN,[1] J.Y. SOHN,[2] S.C. KIM,[2] G.Y. KIM,[3] Y.X. LI,[4] & Y.S. YU[1,2]*

[1] *Electronic Ceramics Center, Dongeui University, Busan 614-714, Korea*

[2] *RIBS and Department of Physics, Dongeui University, Busan 614-714, Korea*

[3] *Department of Urban Engineering, Dongeui University, Busan 614-714, Korea*

[4] *The State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, People's Republic of China*

Submitted February 12, 2003; Revised August 1, 2004; Accepted August 2, 2004

Abstract. Highly *c*-axis oriented Ga-doped ZnO films (GZO) have been grown on sapphire (0001) substrates by pulsed laser deposition (PLD) method. Photoluminescence (PL) spectra indicate that Ga atoms have a large effect on the luminescent properties of ZnO films. PL spectra of GZO films show near band edge (NBE) emissions and broad orange deep-level emissions. The NBE emission shifts to higher energy region and the intensity decreases with the increase of Ga concentration. The blue shift of NBE emission results from Burstein-Moss effect. The quenching of NBE emission is ascribed to the noradiative recombination. The orange emission is related to the oxygen vacancies.

Keywords: Ga-doped ZnO, thin films, photoluminescence

1. Introduction

As a versatile wide band-gap semiconductor material, zinc oxide (ZnO) has a variety of applications including field effect transistors, gas sensors, piezoelectric devices, surface acoustic wave (SAW) devices, solar cells and so on. In recent years, particular attention has been paid to ZnO for its potential applications in blue and ultraviolet light emitting diodes (LEDs) and laser diodes (LDs) due to the large band-gap (3.3 eV) and large exciton binding energy (60 meV) at room temperature. To realize LEDs and LDs, the key challenge is preparing low resistivity *n*-type and *p*-type ZnO thin films, which will lead to the fabrication of *p*-*n* junction. Many groups have focused on making *p*-type ZnO thin films and various methods have been tried [1, 2]. Ga and N co-doping method may be the most promising way to realize *p*-type ZnO from the viewpoint of theoretical calculation [3, 4], and Joseph et al. have reported success in obtaining *p*-type ZnO using Ga and N co-doping method [5].

On the other hand, Ga-doped zinc oxide (GZO) has been widely studied as a type of low resistivity *n*-type transparent conducting oxides (TCO) [6, 7]. A number of studies have been devoted to improving the electrical conductivity and transmittance. Low resistivity and high transmittance ZnO films have been obtained with Ga doping [7, 8]. Although many investigations on GZO thin films have been done so far, only a few authors have touched upon their luminescent properties [9, 10]. A further understanding of the photoluminescence of Ga doped ZnO is essential and helpful for its optical applications.

2. Experimental

The targets used in our experiment were made from high purity ZnO powder (99.99%, Aldrich Chemical Company, Inc, USA) doped with desired amount of Ga_2O_3 (99.99%, Rare Earth Ltd. Co. Japan). The disk-shaped targets of 25 mm in diameter and 2 mm in

*To whom all correspondence should be addressed. E-mail: ysyu@dongeui.ac.kr

thickness were obtained by the iso-static cold press (200 MPa) and then sintered at 1100°C for 6 hours. GZO thin films were deposited on sapphire (0001) substrates by pulsed laser deposition using KrF excimer laser (Lambda Physics LPX, 248 nm). The laser was operated at a pulse rate of 5 Hz and the energy density is maintained at about 1 J/cm^2. The laser beam was focused through 50 cm focal length lens onto a rotating target at 45° angle of incidence. The background oxygen pressure ranged from 100 mTorr to 300 mTorr. The substrate temperature was constant at 400°C during the film growth.

Crystal structures and lattice parameters of the films were characterized by the X-ray diffraction (XRD) method using Cu K_α radiation (Rigaku, D/MAX 2100H). PL measurements were carried out by the excitation of He-Cd laser with 325 nm wavelengths. The carrier concentrations were obtained by Hall Effect measurements (HEM-2000, EGK). All the properties were measured at room temperature.

3. Results and Discussion

GZO films with Ga doping ranging from 0.4 to 3.0 at.% were grown on sapphire (0001) substrates by PLD technique at 400°C and 200 mTorr oxygen pressure. All films show pure wurtzite structure the same as ZnO despite of Ga doping. Figure 1 shows a typical XRD pattern of GZO film doped with 2 at.% Ga. Only the (000*l*) peaks are found along with sapphire (0006) reflection, which indicates that the film has been grown with c-orientation. The lattice constant *c* is calculated from XRD data. Figure 2 exhibits the lattice constant and FWHM ($2\theta/\omega$-scan) for (0002) reflection of GZO films as a function of Ga concentration. With the increase of Ga concentration, the lattice constant *c* and FWHM values gradually increase from 5.204 to 5.230 Å and 0.127 degree to 0.247 degree, respectively. The increase in lattice constant and FWHM can be ascribed to the increase of local strain or point defects associated with Ga atoms. But we should stress that despite high Ga doping, ZnO films exhibit only slight degradation in crystal structure, but no impurity phase appears.

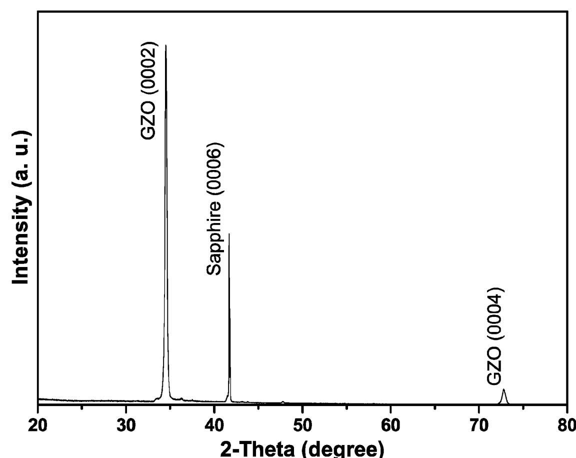

Fig. 1. XRD $\theta/2\theta$ scan of 2 at.% Ga doped GZO film fabricated on sapphire (0001) substrate by PLD method at 400°C and 200 mTorr.

Figure 3 shows PL spectra for GZO thin films with different Ga concentrations grown at 400°C and 200 mTorr. The PL of pure ZnO film fabricated under similar conditions is shown in the figure as a reference. NBE emission and broad deep-level emission are observed from all films. As shown in the figure, the intensity of NBE emission depends strongly on Ga concentration, and it decreases with the increase of Ga concentration. The NBE peak has a slight shift toward higher energy region when Ga concentration increases. Figure 4 represents the variation of NBE emission peak position and the intensity of NBE and deep-level emission with Ga doping concentrations. The NBE peak shifts from 3.264 eV to 3.287 eV when Ga concentration increases from 0.4 to 3.0 at.%. It can be seen that NBE emission quench quickly with the increase of Ga concentration, which implies that nonradiative recombination is introduced with the dopant.

The blue shift of NBE emission is believed to originate from Burstein-Moss effect. We know that Ga is a kind of donor in ZnO. Hall Effect measurements indicate that the carrier concentration for GZO films in our study (10^{19}–10^{20} cm^{-3}) is higher than Mott density (10^{18} cm^{-3}) [11]. So the degenerated electrons enter the conduction band and this results in a shift of the quasi-Fermi level of electrons in the conduction band. The increase of Fermi level in the conduction band of the degenerated semiconductor leads to the energy band widening, called Burstein-Moss band filling effect [12]. The band energy shift ΔE_g is about 20 meV when Ga concentration increase from 0.4 to 3.0% in the present case, which is much smaller than that expected from Burstein-Moss effect. This indicates that the band gap narrowing effects such as electron-electron and electron-impurity interactions should be taken into account [13].

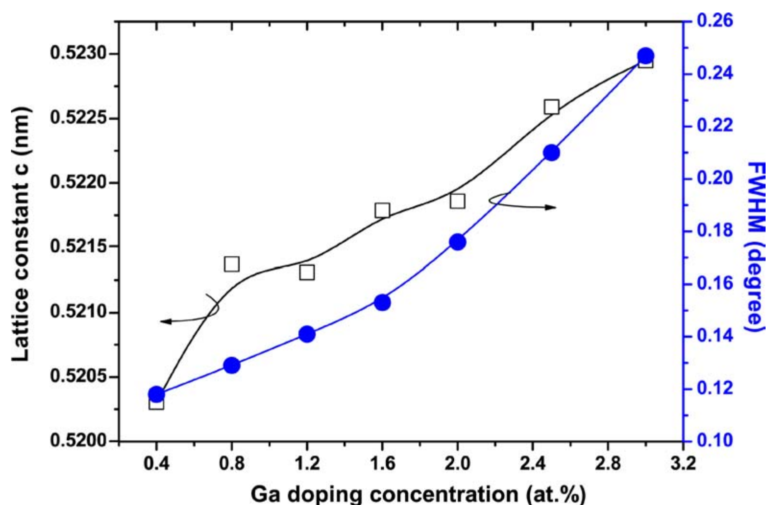

Fig. 2. The lattice constant and $2\theta/\omega$-scan FWHM for (0002) reflex of GZO films prepared at 400°C and 200 mTorr as a function of Ga doping concentration.

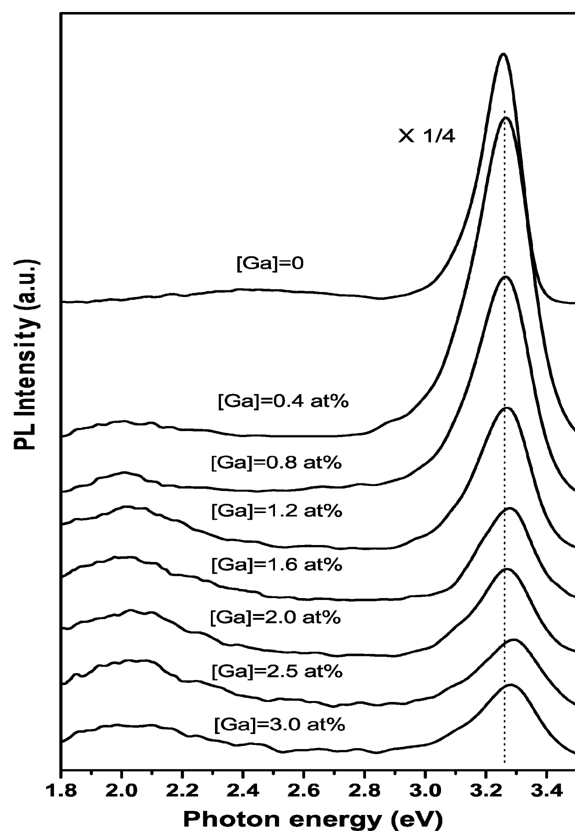

Fig. 3. PL of GZO films with different Ga doping concentrations grown on sapphire (0001) at 400°C and 200 mTorr.

The quenching of NBE emission implies that some nonradiative process occurs in GZO films. A similar phenomenon was observed by Tsang et al. [14] in GaP crystals. They interpreted that such behavior is due to nonradiative Auger recombination processes associated with degenerated electrons, in which the energy released by an electron recombination is immediately absorbed by another electron, and then this energy is dissipated by phonons. Auger process has been thought of as a major reason of nonradiative recombination in semiconductor films [15], quantum well [16] and quantum dots [17]. In wide band gap materials, Auger process depends on the doping level and becomes important when the doping concentration is above Mott density. On the other hand, when Ga doping level is high, the impurity clusters or impurity-defect complexes may also limit the radiative efficiency of GZO films [18].

From Fig. 3 we can also see an interesting phenomenon that all GZO films show broad orange deep-level emissions with maximum at about 2.0 eV, which is different from the green emission of pure ZnO. Compared with PL of pure ZnO (see Fig. 3), the incorporation of Gallium apparently results in a competitive phenomenon that overwhelms the green emission. It should be mentioned that XRD results indicate no contribution of Ga doping to the creation of an impurity phase responsible for the orange emission. Many researchers have reported on the deep-level emission. Although it

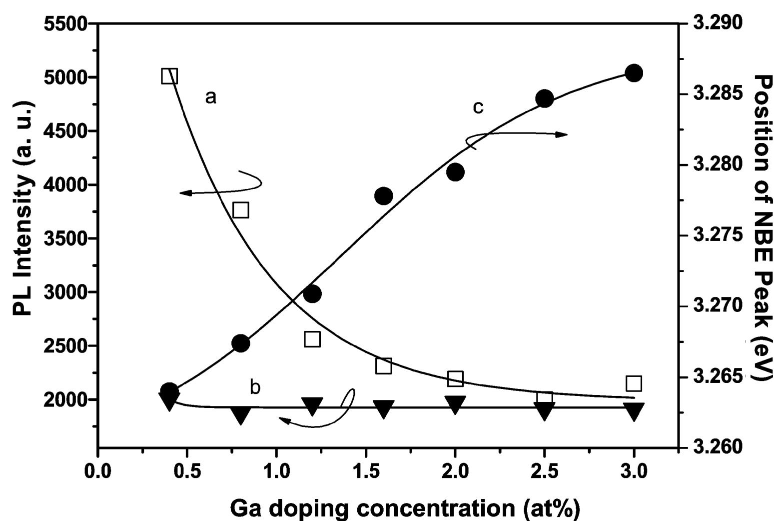

Fig. 4. The NBE emission intensity (a), deep-level emission intensity (b) and the position shifts (c) as a function of Ga doping concentration.

is still controversial, an acceptable explanation of the origin of the green emission is the DA-type transition between donor centers and acceptor centers related to oxygen and zinc defects [19, 20]. While all GZO films in the present case show wide orange deep-level emissions, the deep-level emission intensity shows only slight variation with Ga concentration, which suggests that the deep-level emission has no close dependence on Ga concentration.

To understand the orange emission of GZO films, we fabricated GZO films at different oxygen pressures. Figure 5 gives PL spectra of GZO films with 2.0 at.% Ga doping grown at 400°C and different oxygen pressures. Both NBE emission and broad orange emission are observed for all films. With the increase of oxygen pressure, no obvious change is seen for NBE emission, but the intensity of orange emission decreases. The increase of oxygen pressure results in the decrease of the concentration of oxygen vacancies. So we can conclude that the orange emission is also related to the oxygen vacancies in the GZO films.

The orange emission has also been observed from ZnO doped with lithium, sodium, nitrogen, phosphorous, argon and neon [21, 22]. Shan et al. reported the broad orange emission of Al doped ZnO thin films [23]. We can find that PL characteristics of ZnO doped with different impurities are similar to one another. In all cases, the spectra show a broad orange emission band

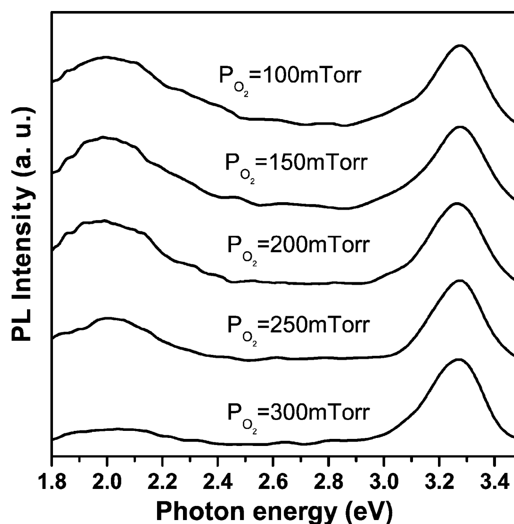

Fig. 5. PL of GZO films prepared at different oxygen pressure and 400°C on sapphire (0001) substrates.

with maximum in the range between 1.8 and 2.2 eV. It is possible that the introduction of the impurity atoms changes the potential energy around the impurity, and results in the variation of the energy levels of oxygen vacancies. The radiative recombination process responsible for the orange emission would take place between the donors associated with oxygen vacancies and the acceptors associated with the native defects adjacent to the impurity.

4. Conclusions

In conclusion, luminescence properties of GZO thin films have been studied. All films show NBE and orange deep-level emissions. The NBE emission peak has a blue shift when the doping concentration increases from 0.4 to 3.0 at.% because of Burstein-Moss band filling effect. The nonradiative recombination process introduced by Ga doping results in the decrease of NBE emission intensity. The orange emission intensity decreases with the increase of ambient oxygen pressure which suggests that the origin of the orange emission could to be related to oxygen vacancies.

Acknowledgments

This work is supported by ECC (Electronic Ceramics Center) at Dong-eui University as RRC·TIC program which is financially supported by KOSEF (Korea Science and Engineering Foundation) and ITEP (Korea Institute of Industrial Technology Evaluation and Planning). We also thank for the supporting of the National Natural Science Foundation of China (NSFC No. 20151003).

References

1. K. Minegishi, Y. Koiwa, Y. Kikuchi, K. Yano, M. Kasuga, and A. Shimizu, *Jpn. J. Appl. Phys.*, **36**, L1453 (1997).
2. Y.R. Ryu, S. Zhu, D.C. Look, J.M. Wrobel, H.M. Jeong, and H.W. White, *J. Cryst. Growth*, **216**, 330 (2000).
3. T. Yamamoto and H.K. Yoshida, *Jpn. J. Appl. Phys.*, **38**, L166 (1999).
4. S.B. Zhang, S.H. Wei, and Alex Zunger, *Phys. Rev. B*, **63**, 075205 (2001).
5. M. Joseph, H. Tabata, and T. Kawai, *Jpn. J. Appl. Phys.*, **38**, L1205 (1999).
6. Kohiki, M. Nishitani, and T. Wada, *J. Appl. Phys.*, **75**, 2069 (1994).
7. G.A. Hirata, J. Mckittrick, J. Siqueiros, A. Lopez, T. Cheeks, O. Contreras, and J.Y. Yi, *J. Vac. Sci. Technol. A*, **14**, 791 (1996).
8. H. Hirasawa, M. Yoshida, S. Nakamura, Y. Suzuki, S. Okada, and K. Kondo, *Sol. Energy Mater.& Sol. Cells*, **67**, 231 (2001).
9. H. Kato, M. Sano, K. Miyamoto, and T. Yao, *J. Cryst. Growth*, **237–239**, 538 (2002).
10. J. Cho, J.B. Nah, M.S. Oh, J.H. Song, K.H. Yoon, H.J. Jung, and W.K. Choi,*Jpn. J. Appl. Phys.*, **40**, L1040 (2001).
11. A.P. Roth, J.B. Webb, and D.F. Williams, *Phys. Rev.*, **25**, 7836 (1982).
12. E. Burstein, *Phys. Rev.*,**25**, 7826 (1982).
13. D. Auvergne, J. Camassel, and H. Mathieu, *Phys. Rev. B*, **6**, 2251 (1975).
14. J.C. Tsang, P.J. Dean, and P.T. Landsberg, *Phys. Rev.*, **173**, 814 (1968).
15. N.K. Dutta and R.J. Nelson, *J. Appl. Phys.*, **53**, 74 (1982).
16. D.J. Jang, M.E. Flatte, C.H. Grein, J.T. Olesberg, T.C. Hasenberg, and T.F. Boggess, *Phys. Rev. B*, **58**, 13047 (1998).
17. V.I. Klimov, A.A. Mikhailovsky, D.W. McBranch, C.A. Leatherdale, and M.G. Bawendi, *Science*, **287**, 1011 (2000).
18. V. Swaminathan, A.T. Macrander, *Materials Aspects of GaAs and InP Based Structures* (Prentice-Hall, New Jersey, 1982), p. 319.
19. D.C. Reynolds, D.C. Look, and B. Jogni, *Solid State Commun.*, **101**, 643 (1997).
20. S.A. Studenikin, N. Golego, M. Cocivera, *J. Appl. Phys.*, **84**, 2287 (1998).
21. A. Ortiz, C. Falcony, J. Hernandez, M. Garcia, and J.C. Alonso, *Thin Solid Films*, **293**, 103 (1997).
22. B.S. Pierce and R.L. Hengehold, *J. Appl. Phys.*, **47**, 644 (1976).
23. F.K. Shan, B.C. Shin, S.C. Kim, and Y.S. Yu, *J. Korean. Phys. Soc.*, **42**, S1374 (2003).