



Evolution of visible luminescence in ZnO by thermal oxidation of zinc films

Y.G. Wang ^a, S.P. Lau ^{a,*}, X.H. Zhang ^b, H.W. Lee ^a, S.F. Yu ^a,
B.K. Tay ^a, H.H. Hng ^c

^a School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

^b Institute of Materials Research and Engineering, Research Link, Singapore 117602, Singapore

^c School of Materials Engineering, Nanyang Technological University, Singapore 639798, Singapore

Received 9 April 2003; in final form 16 May 2003

Abstract

Zinc oxide (ZnO) films were prepared by thermal oxidation of metallic zinc films. The intensities of visible luminescence increase with oxidation time; however the shape and position of the green and yellow luminescence bands are determined by oxidation temperature only and do not vary with oxidation time and excitation laser powers. The green and yellow luminescent bands should originate from different intrinsic defects or defect complexes, which are formed in ZnO at certain temperatures. It suggests that the possibility of donor–acceptor pair recombination as the mechanism responsible for the green and yellow emissions can be excluded.

© 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

ZnO is a versatile material with usages in transducers, varistors and surface acoustic wave devices [1,2]. ZnO is a high efficiency low voltage phosphor in green range for vacuum fluorescent displays and field emission displays; the emission threshold voltage of ZnO is as low as 2.2 eV [3]. Recently, optoelectrical properties of ZnO attract great attentions due to its promising applications as ultraviolet light-emitting diodes and laser diodes [2,4]. The physical mechanisms behind visible luminescence in ZnO are still in controversy, though

extensive experimental and theoretical works have been carried out [5–11]. For the green emission around 2.4 eV, oxygen vacancies [5,11], zinc vacancies [10] and impurities (copper) [9] are considered as most probable candidates. Apart from the green emission, some other emission bands are also observed in ZnO. Yellow emission is an often-reported one. Ohashi et al. [12] observed yellow band around 2.0 eV in polycrystalline ZnO doped with aluminum. Yellow emission was also detected in undoped ZnO film by pulsed laser deposition [13], in lithium doped ZnO film by spray pyrolysis [14] and in single crystal ZnO implanted with hydrogen and sequent annealed in nitrogen ambient [15]. Red emission was reported to exhibit in ion implanted ZnO [16] and in ZnO film by spray

* Corresponding author. Fax: +65-67933318.

E-mail address: esplau@ntu.edu.sg (S.P. Lau).

pyrolysis method prepared at low temperature [17]. The mechanisms behind these emission bands, similar to the green band, are still an open question yet. A better understanding of these visible emissions is essential for designing new phosphor materials and improving its efficiency, and will also do favor to improve crystal quality of ZnO. The investigations about the visible emissions are complicated by the diverse characteristics of ZnO materials used by different researchers; a repeatable material system is highly desired for deep study. In this Letter, ZnO films were prepared by thermal oxidation of metallic zinc films, and the visible luminescence in the films was observed to vary significantly with oxidation temperature. The origins of the green and yellow bands were discussed in the light of the experimental results.

2. Experimental details

Zinc films used for oxidation were deposited by filtered cathodic vacuum arc technique (FCVA) [18]. The base pressure of the deposition chamber is better than 1×10^{-6} Torr, metallic Zn target with purity of 99.99% is used as cathodic target. Zinc film is prepared on quartz substrate with thickness of around 300 nm and then cut into small pieces for oxidation. Oxidation is carried out in a standard Lindberg furnace with a single-well quartz tube in open air. Oxidation temperatures vary from 300 to 900 °C; sample is pushed into the furnace when temperature reaches acquired value, and pulled out quickly when oxidation is finished. The crystal structure of the as-grown zinc and oxidized ZnO films were characterized by X-ray diffraction (XRD, SHIMADZU-6000, Cu-K α radiation). The photoluminescence (PL) spectrum was acquired at room temperature with 325 nm line of a He–Cd laser as an excitation source. The maximum laser power is 16 mW and it can be adjusted with variable attenuator.

3. Results and discussions

Fig. 1 shows the XRD pattern of the as-grown zinc films and ZnO films prepared by oxidation at

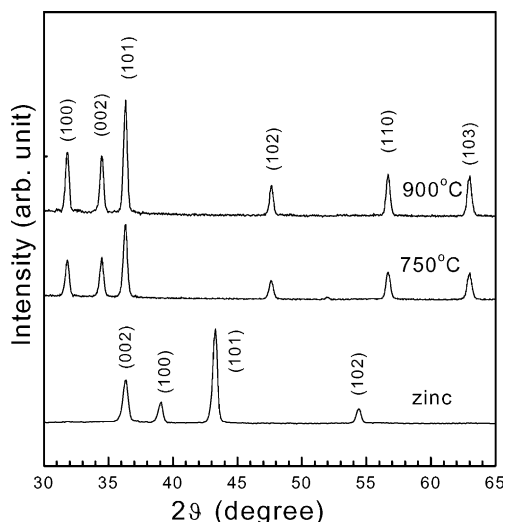


Fig. 1. XRD pattern of the as-grown zinc films and ZnO films prepared by oxidation at 750 and 900 °C for 2 h, respectively.

750 and 900 °C for 2 h. Miller indices are indicated on each diffraction peak. The zinc films are polycrystalline with hexagonal crystal structure. After oxidation, zinc is transformed into ZnO. The ZnO films possess hexagonal wurtzite crystal structure with no preferred orientation. No diffraction patterns of other materials, such as Zn_2SiO_4 , are detected.

Fig. 2 shows the dependence of the PL spectra on the oxidation temperatures, the ZnO films are oxidized for two hours, the spectra are excited with laser power of 8 mW. For clear view, UV and visible parts of the PL spectra are separated into two figures and the curves are shifted vertically. Room temperature UV emission peak is observed at around 3.30 eV, its peak positions shift monotonically to lower energies with increasing of temperature. Its intensities display complicated dependence on oxidation temperature and time, the influence of oxidation conditions on UV emission will be discussed elsewhere [19]. Here, we focus discussions on the evolution of visible luminescence with oxidation conditions. As can be seen from Fig. 2b, the visible emissions display strong temperature dependent. At temperatures from 400 to 750 °C, the visible emission band is composed of a green band around 2.4 eV and a weak red band around 1.85 eV. The intensity of

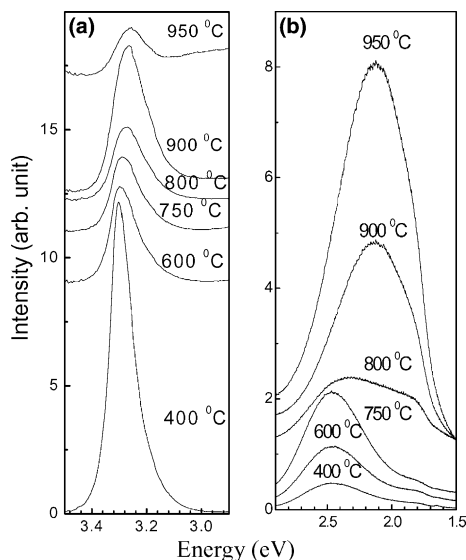


Fig. 2. PL spectra of the ZnO films oxidized at different temperatures for 2 h: (a) the UV band and (b) the visible band.

green band increases with increasing temperature. The red band appears in the spectra of all the samples, the relative intensity of it decreases with increasing of oxidation temperature. Similar red band had been observed and attributed to intrinsic defects in ZnO as oxygen interstitials [16,17]. When oxidation temperature is higher than 750 °C, a variation happens to the visible band, the emission tends to redshift to lower energy. For films oxidized at 900 and 950 °C, the visible emissions are dominated by yellow emission located at around 2.10 eV.

To get better understand of the emissions in green and yellow regions, evolutions of them with oxidation time are checked at two typical temperatures of 750 and 900 °C. Figs. 3a and b show the PL spectra acquired from ZnO films oxidized for different time at temperatures of 750 and 900 °C, respectively. The excitation power is 8 mW. The general trend of them is the same, the intensities of UV emission decrease with time, while the intensities of visible emission increase considerably with oxidation time. The degradation of UV emission is much faster for temperature of 900 °C than that of 750 °C. The positions of visible luminescence are just determined by temperature and are not influenced by oxidation time. The peaks located at 2.4 and 2.1 eV for films prepared at 750 and 900 °C, respectively. In Fig. 4, the visible parts of the two series of spectra are normalized to its maximum value in order to compare the variations of their shape with annealing times. The spectra generally overlap with each other very well for the two temperatures, except the low energy side. The differences at low energy side is due to the decrease of the relative intensities of red emission band with increasing of annealing time, this situation is more obvious for the films oxidized for a short time such as 900 °C for 30 min and 750 °C for 45 min. The position and shape of the visible bands keep nearly unchanged with oxidation time at the investigated temperatures; this implies that the variation of visible band with temperature is not due to the increase of concentration of same type of intrinsic defects, but rather

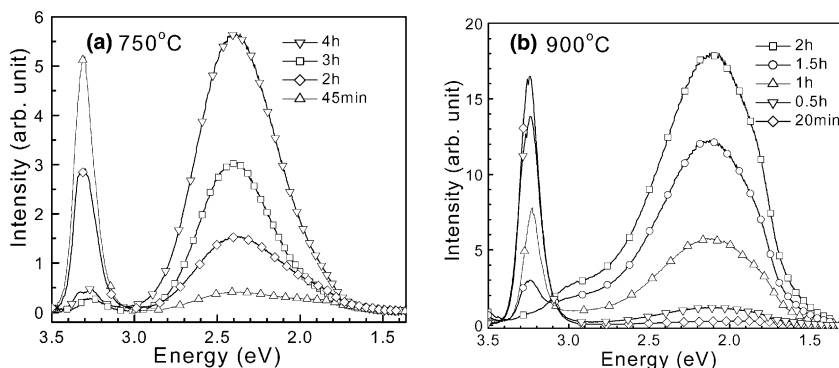


Fig. 3. Variations of PL spectra with time at temperatures of (a) 750 and (b) 900 °C.

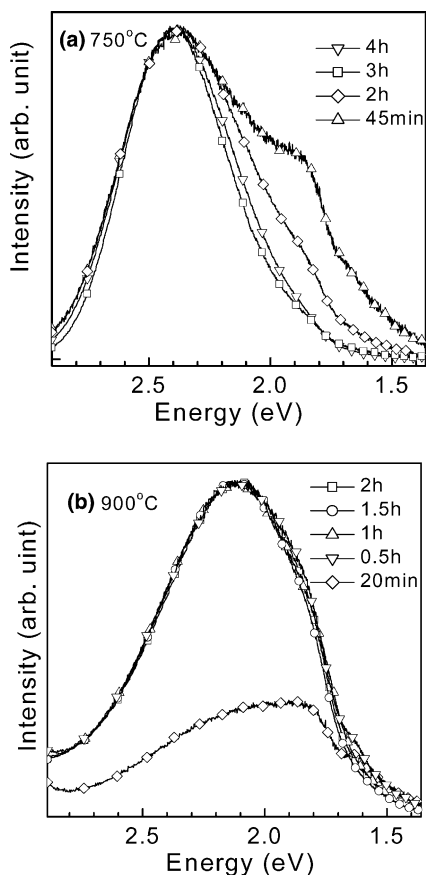


Fig. 4. Normalized figures of the visible parts of the PL spectra as shown in Fig. 3: (a) films annealed at 750 °C and (b) films annealed at 900 °C.

due to the appearance of a new kind of intrinsic defects in ZnO. The formation of these defects is determined by oxidation temperature. ZnO films with yellow color can be prepared under oxidation temperature higher than 800 °C.

Donor–acceptor pair (DAP) recombination is often considered as possible mechanism for the green band in ZnO [6,7]. The energy of the photon resulting from DAP radiative recombination is given by [20]

$$E_{\text{DAP}} = E_{\text{g}} - E_{\text{D}} - E_{\text{A}} + \frac{e^2}{\epsilon r_{\text{DA}}},$$

in which E_{g} is band gap energy, ϵ is the permittivity constant, r_{DA} is the average distance of donor–acceptor pair, E_{D} and E_{A} are donor and acceptor

binding energies, respectively. With increasing excitation intensity, the number of occupied donor and acceptor centers increases and their average distance r_{DA} decreases. As a consequence, the maximum of emission band should shift to the blue due to the Coulomb term in the equation. The dependences of the PL spectra on excitation laser powers are examined for the two ZnO films with green and yellow luminescences that are prepared at 750 and 900 °C, respectively. The results are presented in Figs. 5a and b, the samples were excited by laser powers about 0.4, 1.6 and 16 mW. For easy comparison, the spectra are normalized to their maximum value in the visible luminescent bands. As the excitation intensity increases by

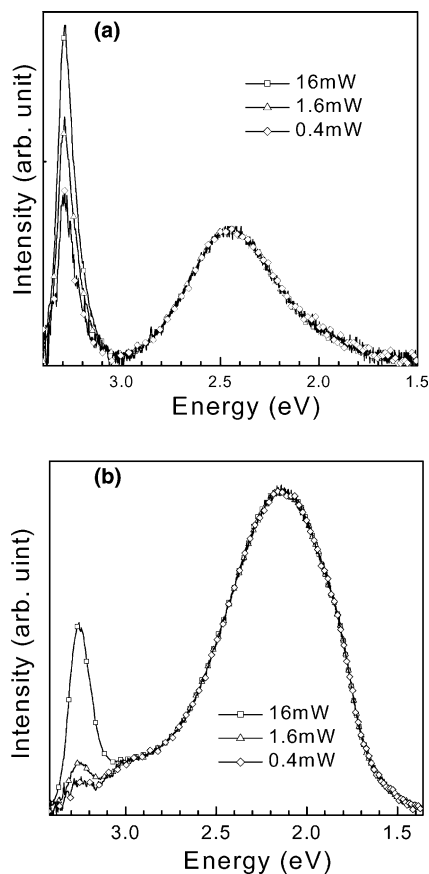


Fig. 5. PL spectra excited by different laser power from two ZnO films prepared at (a) 750 and (b) 900 °C. The excitation power varies from 0.4 to 16 mW. The spectra are normalized to the peak value of the visible emission.

about 40 times, the positions of green and yellow bands do not change, their shapes are also kept exactly the same for various investigated laser powers. Thus it can be safely concluded that DAP as a possible candidate for the visible emission can be excluded at least for our ZnO samples. The relative intensity of the UV emission increases with increasing of excitation power for the two samples as shown in Fig. 5. The improvement of UV emission is due to partial passivation of non-radiative recombination channel and visible emission related defects by high non-equilibrium carrier concentrations induced by high excitation power, this phenomenon is often observed in other semiconductors such as GaN [21].

The shift of visible emission band sometimes is attributed to the variation of band gap [8,13]. When the oxidation temperature increases from 750 to 900 °C, the position of the visible band shifted about 0.3 eV to the low energy side, while the near band edge UV emission shifted about 0.06 eV only. Therefore the band gap variation with oxidation temperature is not the main reason for the shift of visible emission. In fact, temperature dependence experiments on visible emission show that the green band is only weakly coupled to the band properties, when band gap shrinkage with increasing of temperature the position of green band keeps unchanged or even shifts towards opposite direction [22,23]. Our works suggest that the yellow emission band at around 2.1 eV should involve a generation of a new type of defect in ZnO, which is formed at temperature higher than 800 °C. It should be intrinsic defect, because the luminescent behavior of impurities in ZnO should not display such strong temperature dependence. From the time dependent visible spectra as shown in Fig. 4, it can be seen that for the films oxidized at 900 °C, the relative intensity of the green band is very weak. One cannot expect the green emission related defects are not formed at high temperature, so what suppresses the green emission process? One possibility is that at high temperature, green emission related defects are co-produced with other defects and forms defect complex, where the energy level of the complex provides recombination route for yellow light within the band gap of ZnO. Another possible

explanation is that the new defects is formed separately and they induce another energy level in the band gap, and the yellow emission is due to the radiative recombination of carriers between the green related energy level and the newly formed energy level, and probability of this recombination route is much higher than that induces the green emission. To identify the defects responsible for visible luminescence in ZnO, further investigations are still needed.

4. Conclusions

In summary, ZnO films were synthesized by thermal oxidation of metallic zinc films in air. The visible luminescence is dominated by green emission in the films prepared at temperature lower than 750 °C, while a yellow band centered at 2.1 eV appears when temperature is higher than 800 °C. ZnO films with intense green or yellow luminescence band can be prepared at 750 and 900 °C, respectively. The intensities of them increase with oxidation time, and their shape and position change very little with oxidation time and excitation power. Certain kind of intrinsic defects or defect complexes is formed at 900 °C that induces the yellow luminescence.

References

- [1] T.K. Gupta, *J. Am. Ceram. Soc.* 73 (1990) 1817.
- [2] D.C. Look, *Mater. Sci. Eng.* 80 (2001) 383.
- [3] K. Morimoto, in: S. Shionoya, W.M. Ren (Eds.), *Phosphor Handbook*, CRC Press, Cleveland, 1999, p. 561.
- [4] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, *Appl. Phys. Lett.* 70 (1997) 2230.
- [5] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Talant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* 79 (1996) 7983.
- [6] D.C. Reynolds, D.C. Look, B. Jogai, *J. Appl. Phys.* 89 (2001) 6189.
- [7] S.A. Studenikin, M. Cocivera, *J. Appl. Phys.* 91 (2002) 5060.
- [8] A. van Dijken, E.A. Meulenkaamp, D. Vanmaekelbergh, A. Meijerink, *J. Lumin.* 90 (2000) 123.
- [9] N.Y. Garces, L. Wang, L. Bai, N.C. Giles, L.E. Halliburton, G. Cantwell, *Appl. Phys. Lett.* 81 (2002) 622.
- [10] A.F. Kohan, G. Ceder, D. Morgan, C.G. Van de Walle, *Phys. Rev. B* 61 (2000) 15019.
- [11] S.B. Zhang, S.-H. Wei, A. Zunger, *Phys. Rev. B* 63 (2001) 075205.

- [12] N. Ohashi, T. Nakata, T. Sekiguchi, H. Hosono, M. Mizuguchi, T. Tsurumi, J. Tanaka, H. Haneda, *Jpn. J. Appl. Phys.* 38 (1999) L113.
- [13] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, *Appl. Phys. Lett.* 78 (2001) 2285.
- [14] A. Ortiz, C. Falcony, J. Hernandez, M. Garcia, J.C. Alonso, *Thin Solid Films* 293 (1997) 103.
- [15] K. Ip, M.E. Overberg, Y.M. Heo, et al., *Appl. Phys. Lett.* 81 (2002) 3996.
- [16] B.J. Pierce, R.L. Hengehold, *J. Appl. Phys.* 47 (1976) 644.
- [17] S.A. Studenikin, N. Golego, M. Cocivera, *J. Appl. Phys.* 84 (1998) 2287.
- [18] X.L. Xu, S.P. Lau, J.S. Chen, G.Y. Chen, B.K. Tay, *J. Cryst. Growth* 223 (2001) 201.
- [19] Y.G. Wang, S.P. Lau, et al., *J. Appl. Phys.* (in press).
- [20] C.F. Kingshirm, in: *Semiconductor Optics*, Springer, Berlin, 1995, p. 246.
- [21] S.Y. Karpov, Y.N. Makarov, *Appl. Phys. Lett.* 81 (2002) 4721.
- [22] F. Leiter, H. Zhou, F. Henecker, A. Hofstaetter, D.M. Hofmann, B.K. Meyer, *Physica B* 308–310 (2001) 980.
- [23] T. Sekiguchi, N. Ohashi, Y. Terada, *Jpn. J. Appl. Phys.* 36 (1997) L289.