



Photoluminescence Studies of ZnO thin films grown by atomic layer epitaxy

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Abstract

ZnO thin films have been grown on sapphire substrates by the atomic layer epitaxy technique using diethylzinc and H₂O as reactant gases at substrate temperatures of 170°C and 400°C and annealed at temperatures of 800–1000°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. Based on the full-width at half-maximum measurement of the free exciton emission of 67.54 meV have been made at room temperature. Both the PL intensity peaks in the UV light and visible light regions are increased by annealing the ZnO film in an oxygen atmosphere. In contrast, only the PL intensity peak in the UV light region is selectively increased by annealing it in a nitrogen atmosphere. Also, the ZnO film deposited at 170°C shows better PL characteristics than that deposited at 1000°C.
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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, low power threshold for optical pumping and highly efficient UV emission resulting from a large exciton binding energy of 60 meV. Moreover, ZnO is thermally

and chemically stable in ambient air. The versatile physical properties of ZnO are applicable as a transparent conductive contact [1], thin-film gas sensor [2,3], varistor [4], surface electroacoustic wave device [5], UV laser [6,7] and others [8]. ZnO has been subject to growing interest, especially since Service reported its potential application as an UV laser diode [9]. Recently, optically pumped stimulated emission and lasing of ZnO have been demonstrated, even at room temperature [10–12]. It is essential to investigate the photoluminescence property of the semiconductor in developing a new semiconductor material for the fabrication of

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optoelectronic devices such as laser diode (LD) and light emitting diode (LED).

A variety of techniques have been used to grow ZnO thin films including sputtering [12], molecular beam epitaxy (MBE) [13], metal organic chemical vapor deposition (MOCVD) [14], pulsed laser deposition (PLD) [15] and spray pyrolysis [16]. The photoluminescence (PL) properties of ZnO thin films are dependent on the growing method, but they are more dependent on the postannealing process. The PL properties of ZnO thin films can be significantly enhanced by postannealing. Particularly they are strongly dependent on annealing process conditions such as substrate temperature, process time, and atmosphere and the annealing method such as furnace annealing (FA) and rapid thermal annealing (RTA).

In this communication, we report the effect of annealing temperature on the PL property of the ZnO thin film grown on the sapphire substrate by atomic layer epitaxy (ALE). ALE is a very attractive technique for growing thin epitaxial films. It is a self-limiting growth process with controlled surface reaction where the growth rate is only dependent on the number of growth cycle and the lattice parameter of materials. ALE growth process has many advantages including accurate thickness control, the coverage of large area substrates, excellent conformality, large batch capability, and capability to produce sharp interfaces. Besides them ALE is beneficial for the growth of the films at lower temperatures than conventional CVD techniques [17]. ALE sometimes is also called atomic layer deposition (ALD), and there are many reports on the quality (structures) of ALD ZnO films as conductive layers for solar cell applications [18–24]. Yet, the ALE technique has never been applied to epitaxial growth of ZnO in spite of its merits written above and there has been nearly no report on the photoluminescence property of ALE ZnO thin films.

2. Experimental

ZnO films were deposited on sapphire substrates using the ALE technique. Diethylzinc (DEZn) and

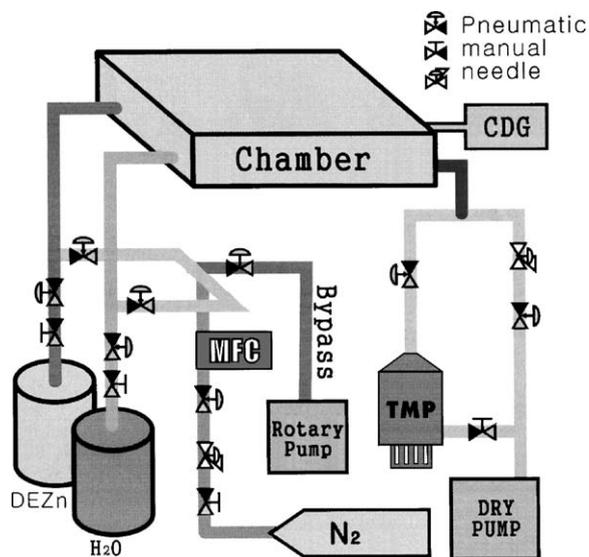


Fig. 1. A schematic of the ALE system.

H₂O were kept in reservoirs 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 the purge between the reactants. The substrate temperatures were varied between 170°C and 400°C. The pressure in the chamber during the deposition was varied between 0.3–0.5 Torr. The thickness of the ZnO films grown by ALE was around 200 nm. A 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, ZnO films have been annealed in an oxygen atmosphere for 1 h or in a nitrogen atmosphere for 3 min by rapid thermal annealing (RTA) in the temperature range from 600°C to 1000°C.

3. Results and discussion

PL spectra of ZnO thin films grown by ALE and then annealed at temperatures of 600°C–1000°C

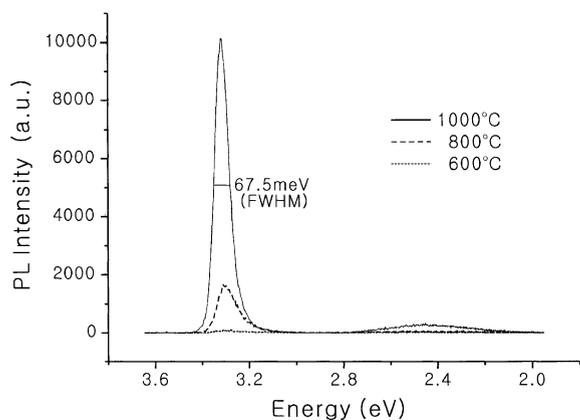


Fig. 2. PL spectra of ZnO films annealed at 1000°C, 800°C and 600°C for 1 h in an oxygen atmosphere after deposition at the substrate temperature of 170°C.

are shown in Fig. 2. For the sample annealed at 1000°C a sharp peak is found around the energy of 3.3 eV equivalent to the wavelength of 3700–3800 Å indicating a UV emission peak. This peak is known to be caused by excitons [25,26]. The full-width at half-maximum (FWHM) as small as 67.5 meV proves a high quality ZnO film has been obtained by ALE and postannealing at 1000°C. The ZnO samples were prepared using a normal ALE process condition and light emission was not detected for the as-grown ZnO film. As the annealing temperature increased, the PL intensity peak in the UV region (around 3.3 eV) increased significantly and the one in the visible light region (around 2.4 eV) increased slightly.

The FWHM of the PL intensity peak in the UV light region decreased to 67.5 meV desirably by annealing the sample in an oxygen atmosphere at 1000°C for 1 h. The ALE process is usually made at a low temperature so that no chemical reaction may occur between the chemical species in the same precursor. Therefore, the crystalline quality of the as-grown film may not be satisfactory because of insufficient thermal energy provision. However, our experimental results show that the light-emitting property of the film can be significantly enhanced by annealing.

Various mechanisms have been proposed for the green luminescence of ZnO. Vanheusden et al. [24] reported that singly ionized oxygen vacancies (V_{O}^{\bullet})

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}^{\bullet}), and the doubly ionized oxygen vacancy ($V_{\text{O}}^{\bullet\bullet}$); and only the singly ionized oxygen vacancy (V_{O}^{\bullet}) can act as luminescent centers [27].

The ZnO film grown by ALE nearly does not have Zn–Zn bonds but Zn–O bonds; since ALE is a low temperature process, it does not emit light in the wavelength region of visible light. To confirm this fact a ZnO film containing Zn–Zn bonds was grown intentionally and the PL spectroscopic analysis for the film was performed. The ZnO film sample containing Zn–Zn bonds was prepared by ALE without flowing the purge gas at all during the purge steps. Fig. 3 shows a PL intensity peak in the visible light region as well as the one in the UV light region for this sample after annealing in a nitrogen atmosphere at 850°C for 3 min. This result confirms that light emission of ZnO in the visible light region is minimized by growing it by ALE.

The low-temperature ALE offers not only an advantage that it nearly does not form Zn–Zn bonds but also a disadvantage that the crystallinity of the ZnO film may not be satisfactory. To see the effect of increasing the substrate temperature in the ALE process on the PL property of ZnO or the quality of the ZnO film at 400°C which is beyond the upper limit of the ALE process temperature

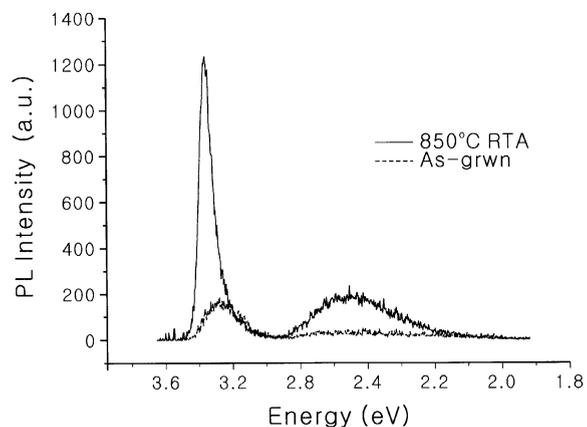


Fig. 3. PL spectra ZnO film deposited at the substrate temperature of 200°C without purge gas.

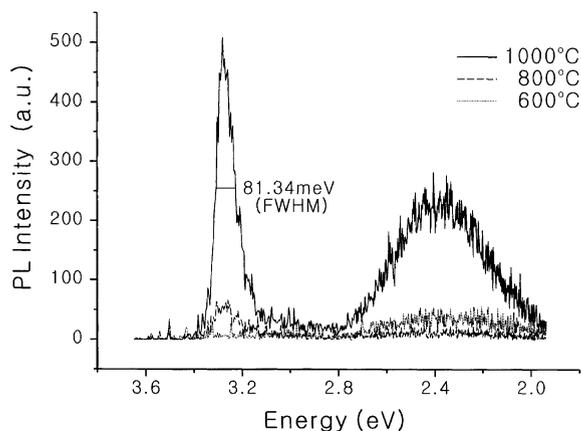


Fig. 4. PL spectra of ZnO films annealed at 1000°C, 800°C and 600°C for 1 h in an oxygen atmosphere after deposition at the substrate temperature of 400°C.

range, what is called ALE window and annealed in an oxygen atmosphere for 1 h. The PL spectra for this sample after annealing at 600, 800 and 1000°C are shown in Fig. 4. There seems to be nearly no difference in PL property or crystallinity because the PL peak height for the ZnO film grown at 400°C and then annealed at 600 or 800°C (Fig. 4) is almost the same as that for the ZnO film grown at 170°C (Fig. 3). The PL spectroscopic analysis results suggest that the annealing temperature should be quite high. The effect of the annealing temperature on the PL property of the ZnO film seems to be negligible at 600 or 800°C, but annealing at 1000°C has increased the PL intensity peak height significantly.

Fig. 5 shows the PL spectra for the ZnO films grown at 400°C and then annealed in a nitrogen atmosphere at different temperatures for 3 min. It suggests that annealing in a nitrogen atmosphere at the temperature as high as 800°C improves the PL intensity in the UV region without increasing the one in the visible light region differently from annealing in an oxygen atmosphere which increases both the PL intensity peaks in the UV and visible light regions.

4. Conclusion

In this paper, we have presented effects of annealing on the photoluminescence properties of

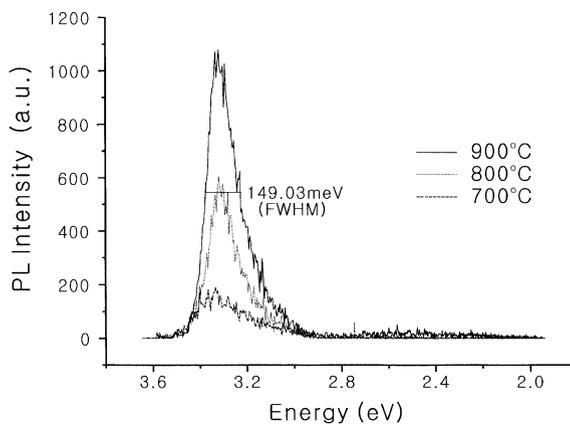


Fig. 5. PL spectra of samples annealed by RTA process at 700°C, 800°C and 900°C for 3 min in a nitrogen atmosphere after deposition at the substrate temperature of 400°C.

ZnO films prepared by the ALE technique. The PL characteristics were significantly enhanced by annealing treatment. A strong peak was obtained in the green band for the ZnO thin film deposited at 400°C due to the large amount of oxygen vacancies caused by excess Zn atoms, while nearly no peak appeared for the one deposited at 170°C. Both the PL intensity peaks in the UV light and visible light regions are increased by annealing the ZnO film in an oxygen atmosphere. In contrast, only the PL intensity peak in the UV light region is selectively increased by annealing it in a nitrogen atmosphere.

Acknowledgements

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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. Aiyer, *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 Regular Papers Short Notes and Review Papers* 36 (1997) 1169.
- [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] 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.
- [11] 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.
- [12] K.H. Kim, K.C. Park, D.Y. Ma, *J. Appl. Phys.* 81 (1997) 7764.
- [13] A. Yamamoto, T. Kido, T. Goto, Y.F. Chen, T. Yao, D.C. Look, *Appl. Phys. Lett.* 75 (1999) 469.
- [14] C.R. Gorla, N.W. Emanetoglu, S. Liang, W.E. Mayo, Y. Lu, M. Wraback, H. Shen, *J. Appl. Phys.* 85 (1999) 2595.
- [15] J.F. Muth, R.M. Kolbas, A.K. Sharma, S. Oktyabrsky, J. Narayan, *J. Appl. Phys.* 85 (1999) 7884.
- [16] S.A. Studenikin, N. Golego, M. Cocivera, *J. Appl. Phys.* 84 (1998) 2287.
- [17] T. Suntola, *Mater. Sci. Rep.* 4 (1989) 261.
- [18] H. Sato, T. Minami, S. Takata, T. Miyata, M. Ishii, *Thin Solid Films* 236 (1993) 14.
- [19] V. Lujala, J. Skarp, M. Tammenmaa, T. Suntola, *Appl. Surf. Sci.* 82/83 (1994) 34.
- [20] B. Sang, A. Yamada, M. Konagai, *Solar Energy Mater. Solar Cells* 49 (1977) 19.
- [21] K. Saito, Y. Watanabe, K. Takahashi, T. Matsuzawa, B. Sang, M. Konagai, *Solar Energy Mater. Solar Cells* 49 (1997) 187.
- [22] A. Yamada, B. Sang, M. Konagai, *Appl. Surf. Sci.* 112 (1997) 216.
- [23] E.B. Yous, J. Fouache, D. Lincot, *Appl. Surf. Sci.* 153 (2000) 223.
- [24] Y. Yamato, K. Saito, K. Takahashi, M. Konagai, *Solar Energy Mater. Solar Cells* 65 (2001) 125.
- [25] M.H. Huang, Y.Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [26] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, M.Y. Shen, T. Goto, *Appl. Phys. Lett.* 75 (1998) 1038.
- [27] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, *J. Appl. Phys.* 79 (1996) 7983.