

Photoluminescence Characteristics of ZnO Nano Needle-like Rods grown by the Hot Wall Epitaxy Method

Sung-Hwan Eom

KoMiCo,

Sinmosan-dong, Anseong-si, Gyeonggi 456-390, Korea

Yong Dae Choi^a

*Department of Optical and Electronic Physics, Mokwon University,
800 Doan-dong, Seo-gu, Daejeon 302-729, Korea*

^aE-mail: ydchoi@mokwon.ac.kr

(Received June 27 2007, Accepted October 10 2007)

We investigated photoluminescence characteristics of ZnO nano needle-like rods grown on a *c*-plane Al₂O₃ substrate by the hot wall epitaxy method. The nano-rods were vertically well aligned along the ZnO *c*-axis. The diameters of the ZnO nano-rods ranged from 20 nm to 30 nm and their lengths were between 600 and 700 nm. In the photoluminescence spectrum at 10 K, the exciton emission bound to the neutral donor dominated while defect related emission was weakly observed. With a further increase of temperature, the free exciton emission appeared and eventually became dominant at room temperature.

Keywords : ZnO, Nano needle-like rod, Photoluminescence, Hot wall epitaxy

1. INTRODUCTION

In recent years, ZnO has attracted considerable attention as a promising material for application in short wavelength optical and opto-electronic devices such as lasers and photodetectors operating in the UV spectral range.

ZnO has a wide band gap of 3.37 eV at room temperature with a hexagonal wurtzite structure. Furthermore, its exciton binding energy of 60 meV is much larger than that of GaN[1-3], which is commercially used to fabricate blue optoelectronic devices. For these reasons, ZnO affords the possibility to achieve efficient excitonic laser action at room temperature.

There have been many reports on the growth of ZnO and several techniques have been proposed, including chemical vapor deposition[4], RF magnetron sputtering [5], pulsed laser deposition (PLD)[6], and thermal evaporation[7]. In addition to the growth of high quality ZnO films, characterization of the structural, electrical, and optical properties have been reported in efforts to determine the optimal growth conditions[8-10]. However, ZnO nano-rods grown by the hot wall epitaxy (HWE) method have not yet been reported. The advantages of this method are as follows: (i) the product

cost is lower than that of other techniques; (ii) the status is simple; and (iii) the source, wall, and substrate temperatures can be controlled independently[11].

In the present work, nano needle-like rods (hereafter referred to as nano-rods) of ZnO are grown on a *c*-plane Al₂O₃ substrate and their structural and optical properties are investigated by X-ray diffraction (XRD), field emission scanning microscopy (FE-SEM), and photoluminescence (PL) spectroscopy.

2. EXPERIMENTAL PROCEDURE

The ZnO nano-rods were grown on the *c*-plane Al₂O₃ substrates by the HWE method. HWE system is designed to maintain near-thermal equilibrium by installing a hot wall between the source and the substrate. The position of the substrate is just above the upper end of the hot wall. The hot wall can produce a well-collimated beam of the molecules. In addition, the flux intensity and the kinetic energy of the molecules can - to some extent - be adjusted independently by choosing a wall temperature different from the source temperature[11].

The source material used in this study was 5N polycrystalline ZnO powder. The *c*-plane Al₂O₃ substrates

were ultrasonically cleaned by trichloroethylene, acetone and methanol, in sequence, for 15 min each. They were then chemically etched in a hot $\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4=3:1$ solution for 10 min and rinsed by flushing deionized water. After being dried with high purity Ar gas, they were placed on a substrate holder in the HWE system. Prior to the growth, the substrate was heated at 590°C under approximately 2×10^{-7} Torr pressure for 20 min in order to remove remaining impurities and oxide layers on the substrate surface. The growth conditions were as follows: 1050°C source, 710°C wall, and 540°C substrate temperature, respectively. The growth period was 3 hr under 3×10^{-6} Torr.

The crystal structures and surface morphologies were investigated using XRD and FE-SEM. PL measurements were carried out in a temperature range from 10 K to 300 K using a He-Cd laser with the 325 line as an excitation source. The luminescence from the sample was detected using a GaAs photomultiplier tube with a 1 m double monochromator (Jobin-Yvon U1000).

3. RESULTS AND DISCUSSION

According to the known hexagonal ZnO diffraction peaks (JCPDS card No. 36-1451), the XRD spectra of ZnO nano-rods grown under the above conditions show only (002) and (004) ZnO peaks and the substrate (006) Al_2O_3 peak, as shown in Fig. 1. This implies that the ZnO nano-rods are perfectly oriented to the c -axis, which is perpendicular to the Al_2O_3 substrate. The full width at the half maximum (FWHM) of the (002) peak is as small as 0.16° , which is comparable with that of ZnO nano-rods grown by metalorganic chemical vapor deposition[12] and PLD[13]. No impurity peaks such as metallic Zn or other non-stoichiometric Zn compounds were observed, reflecting the high purity of the material. On the other hand, the (002) peak is slightly shifted to the higher angle side relative to that of bulk ZnO. This indicates that the ZnO nano-rods are influenced by residual strain in the nano-rods.

The surface morphology of ZnO nano-rods is shown in Fig. 2. It is found that the grown ZnO nano-rods have a vertically well-aligned orientation. With regard to the growth orientation, Laudies *et al.* suggested that the growth velocity of the $\langle 001 \rangle$ direction is much higher than that of other directions, i.e., $\langle 101 \rangle$ and $\langle 100 \rangle$ [14]. Recently, Park *et al.* grew sharp-tipped nano-needle shape ZnO via MOCVD. They suggested that this shape originated from a higher growth rate along the $\langle 001 \rangle$ direction than that along the in -plane[15]. Based on these results, it is thought that the vertically aligned ZnO nano-rods obtained herein result from the higher growth rate of the $\langle 001 \rangle$ direction.

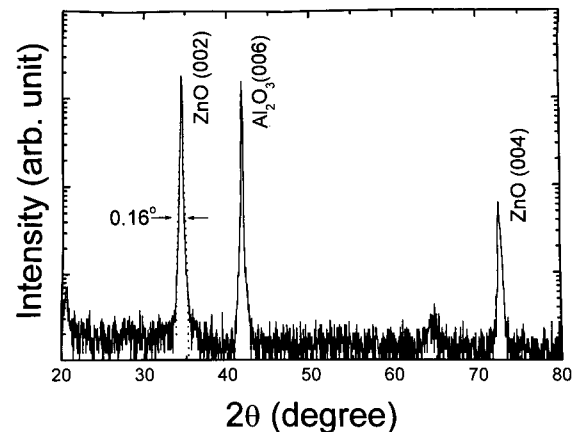


Fig. 1. XRD pattern of ZnO nano-rods grown on the c -plane Al_2O_3 substrate.

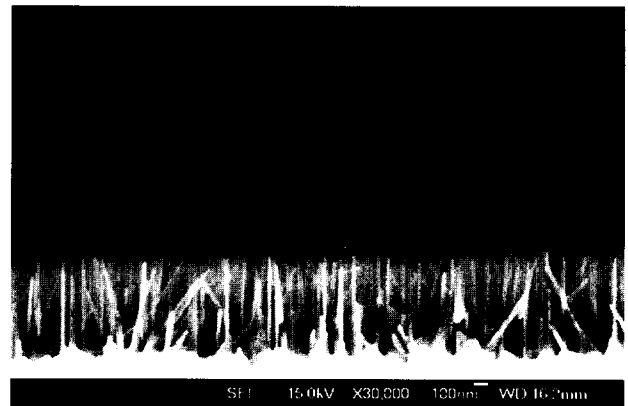


Fig. 2. FE-SEM image of as-deposited ZnO nano-rods on the c -plane Al_2O_3 substrate.

Figure 3 shows the room temperature PL spectrum, where two emission bands (denoted by A and B) are observed. Among these bands, the A band (3.30 eV) may be attributed to the free exciton emission (band edge emission, NBE)[15] while the broad band B (2.35 eV) is known to be associated with oxygen vacancies and Zn interstitials in the ZnO lattice[16]. It should be noted that the green emission band was comparable with NBE in intensity. According to previous results, it is well known that the green emission intensity strongly depends on the diameter size of the nano-material. Briefly, a decrease in the diameter of nano-rods and/or nano-wire results in an increase in the amount of oxygen vacancies. Yao *et al.* have grown three types of nano-materials, nano-wires, nano-ribbons, and nano-rods, by the simple method of thermal evaporation of ZnO powder mixed with graphite[17]. They found that the intensity of the NBE

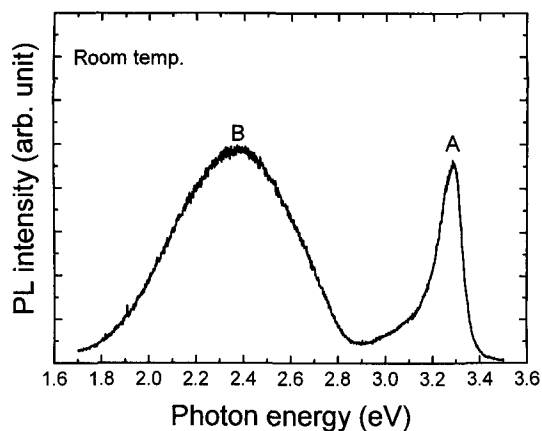


Fig. 3. Room temperature PL spectrum.

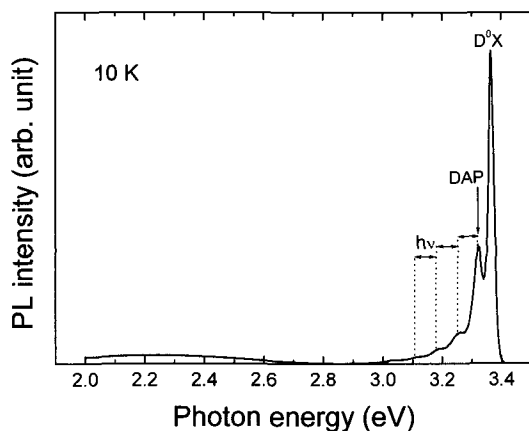


Fig. 4. PL spectrum taken at 10 K.

emission was remarkably enhanced in the sequence of nano-wire, nano-ribbon, and nano-rod, whilst the green emission band was decreased. This suggests that a great fraction of oxygen vacancies or Zn interstitials is included in thinner ZnO nano-wires. Similar results have also been reported by Huang *et al.*[16].

We also confirmed this trend in the nano-rods grown in the present study (results not shown here). In the present work, the diameter of the rods is approximately 20-30 nm, which is about 1/10 smaller than that obtained by Yao *et al.*[17]. However, the ratio of the NBE emission to the green emission is nearly 1, which is about two times that found by Yao *et al.*. This could be explained in terms of the influence of growth ambience. Yao *et al.* synthesized ZnO nano-wires in a quartz tube where one end was open to the atmosphere. Under these conditions, impurities could be introduced of during growth, which might have influenced the green emission.

Figure 4 depicts the PL spectrum measured at 10 K. The spectrum is composed of several emissions: D^0X (3.365 eV), DAP (3.317 eV) and DAP related three LO

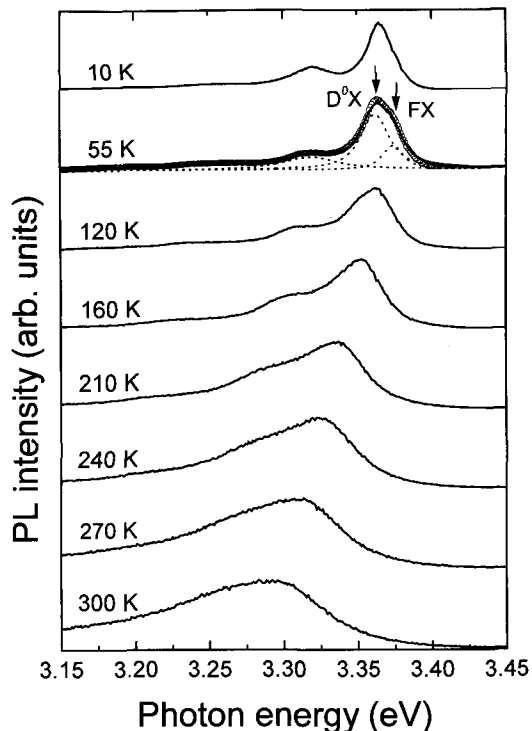


Fig. 5. Thermal quenching spectra of ZnO nano-rods.

phonon emissions (3.324 eV, 3.317 eV and 3.309 eV). On the other hand, a deep emission, due to singly ionized oxygen vacancies, was weakly observed and the UV-to-green emission ratio was about 35.

Figure 5 shows typical PL spectra for the ZnO nano-rods taken at various temperatures. As the temperature is increased, the D^0X emission shifted to lower energy accompanied by a decrease in intensity. With a further increase of temperature, the free exciton shoulder becomes clearly visible and subsequently dominantly appears at higher temperature. Generally, as the temperature is increased, the interaction between the free excitons and the neutral donor bound excitons is gradually reduced and the excitons bound to donors are subsequently freed. Finally, free exciton emission dominates at higher temperature. Consequently, these two emission peaks become overlapped and the D^0X emission was difficult to resolve upon increasing of the temperature to 160 K.

The temperature variations of the peaks of the free excitons and D^0X emission are shown in Fig. 6. Since the temperature dependence of both free and bound exciton emissions exhibit very similar behavior, as shown in Fig. 6, the D^0X emission involves a shallow donor level. The temperature-induced variation of the band gap energy E_g is generally described by Varshni's empirical express[18]

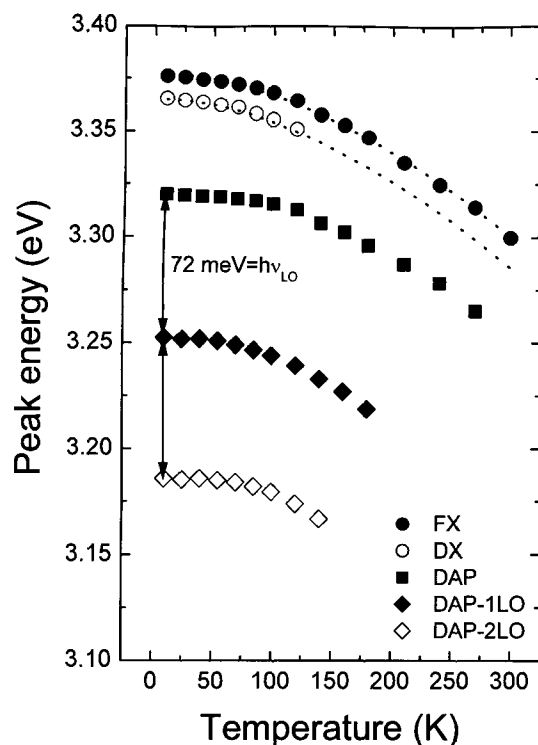


Fig. 6. Temperature dependence of the free and bound exciton emission to neutral donor.

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} \quad (1)$$

where $E_g(0)$ is the band gap energy at 0 K, and α and β are Varshni's thermal coefficient and Debye temperature, respectively; these parameters are to be determined by curve fitting to the experimental data. Since the temperature behavior of the free exciton emission is similar to that of the band gap energy, E_g can be replaced with E_{FX} for the free exciton emission. The dotted lines indicate the fit of the data to Eq. (1). The temperature variation of E_{FX} by Eq. (1) agrees well with the experimental results. The obtained α and β are 9.0×10^{-4} eV/K and 1210 K, respectively, for the two emission lines. The value of $E_{FX}(0)$ is estimated to be 3.378 eV for the free exciton emission and 3.365 eV for the D^0X emission, respectively. The free exciton emission energy is in agreement with the previous results. Furthermore, the binding energy of the D^0X emission of 13 meV is in the range of 10-20 meV. This value is in agreement with the previously reported binding energy of exciton to defect-pair complexes, which is also known to be in the range of 10 to 20 meV[19].

4. CONCLUSION

We have grown ZnO nano-rods on a *c*-plane Al_2O_3

substrate using the HWE method and subsequently investigated the PL properties. Nano-rods vertically well aligned to the substrate normal were confirmed from FE-SEM and XRD spectra. The typical nano-rod sizes were 20-30 nm in diameter and 600-700 nm in length, respectively. The room temperature PL emission was found to consist of two emission bands, 3.29 eV due to the free exciton, and a green emission band at 2.35 eV due to oxygen vacancies or unintentionally introduced defects. From fitting the temperature-induced variation of the free exciton and D^0X emission to Varshni's empirical formula, the values of α and β were found to be 9×10^{-4} eV/K and 1210 K, respectively, and the $E(0)$ values were determined as 3.378 eV and 3.365 eV for the two emission lines, respectively.

ACKNOWLEDGMENTS

This work was supported by a Korea Research Foundation grant(KRF-2002-070-C00036).

REFERENCES

- [1] D. C. Look, "Recent advances in ZnO materials and devices", *Mater. Sci. Eng.*, Vol. B 80, p. 383, 2001.
- [2] P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, "Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin films at room temperature", *Solid-State Commun.*, Vol. 103, p. 459, 1997.
- [3] D. M. Bagnall, Y. R. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, "Optically pumped lasing of ZnO at room temperature", *Appl. Phys. Lett.*, Vol. 70, p. 2230, 1997.
- [4] D.-I. Suh, S.-K. Lee, and B.-G. Ahn, "Synthesis and characterization of branched-structure ZnO nanowires grown by using a two-step seeding method", *Sae Mulli(The Korean Physical Society)*, Vol. 54, No. 4, p. 351, 2007.
- [5] H.-J. Jin, S.-J. So, and C.-B. Park, "Defect analysis via photoluminescence of p-type ZnO:N thin film fabricated by RF magnetron sputtering", *J. of KIEEME(in Korean)*, Vol. 20, No. 3. p. 202, 2007.
- [6] E. S. Shim, H. S. Kang, J. S. Kang, S. S. Pang, and S. Y. Lee, "p-n heterojunction composed of n-ZnO/p-Zn-doped InP", *Trans. EEM*, Vol. 3, No. 1, p. 1, 2002.
- [7] B. H. Kong, T. E. Park, and H. K. Cho, "Shape control and characterization of one-dimensional ZnO nanostructures through the synthesis procedure", *J. of KIEEME(in Korean)*, Vol. 19, No. 1. p. 13, 2006.
- [8] Y. G. Wang, S. P. Lau, H. W. Lee, S. F. Yu, B. K. Tay, X. H. Zhang, and H. H. Hng, "Photoluminescence

- study of ZnO films prepared by thermal oxidation of Zn metallic films in air”, *J. Appl. Phys.*, Vol. 94, p. 354, 2003.
- [9] D. B. Yang, Y. F. Chan, and N. Wang, “Formation of ZnO nanostructures by a simple way of thermal evaporation”, *Appl. Phys. Lett.*, Vol. 81, p. 757, 2002.
- [10] K. Ogata, T. Kawanishi, K. Maejima, K. Sakurai, S. Fujita, and S. Fujita, “Improvements of ZnO qualities grown by metal-organic vapor phase epitaxy using a molecular beam epitaxy grown ZnO layer as a substrate”, *Jpn. J. Appl. Phys.*, Vol. 40, p. L657, 2001.
- [11] A. Lopez-Otero, “Hot-wall epitaxy”, *Thin Solid Films*, Vol. 49, No. 1, p. 3, 1978.
- [12] H. Yuan and Y. Zhang, “Preparation of well-aligned ZnO whiskers on glass substrate by atmospheric MOCVD”, *J. Cryst. Growth*, Vol. 263, p. 119, 2004.
- [13] Y. Sun, G. M. Fuge, and M. N. R. Ashfold, “Growth of aligned ZnO nanorod arrays by catalyst-free pulsed laser deposition methods”, *Chem. Phys. Lett.*, Vol. 396, p. 21, 2004.
- [14] R. A. Laudise, E. D. Kolb, and A. J. Caporaso, “Hydrothermal growth of large single crystals of zinc oxide”, *J. Am. Ceram. Soc.*, Vol. 47, p. 9, 1964.
- [15] W. I. Park, G.-C. Yi, M. Kim, and S. J. Pennycook, “ZnO nanoneedles grown vertically on Si substrates by non-catalytic vapor-phase epitaxy”, *Adv. Mater.*, Vol. 14, p. 1841, 2002.
- [16] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, “Catalytic growth of Zinc Oxide nanowires by vapor transport”, *Adv. Mater.*, Vol. 13, p. 113, 2001.
- [17] B. D. Yao, Y. F. Chan, and N. Wang, “Formation of ZnO nanostructures by a simple way of thermal evaporation”, *Appl. Phys. Lett.*, Vol. 81, p. 757, 2002.
- [18] Y. P. Varshni, “Temperature dependence of the energy gap in semiconductors”, *Physica*, Vol. 34, p. 149, 1967.
- [19] D. W. Hamby, D. A. Lucca, M. J. Klopstein, and G. Cantwell, “Temperature dependent exciton photoluminescence of bulk ZnO”, *J. Appl. Phys.*, Vol. 93, p. 3214, 2003.