

The properties of ZnO photoluminescence at and above room temperature

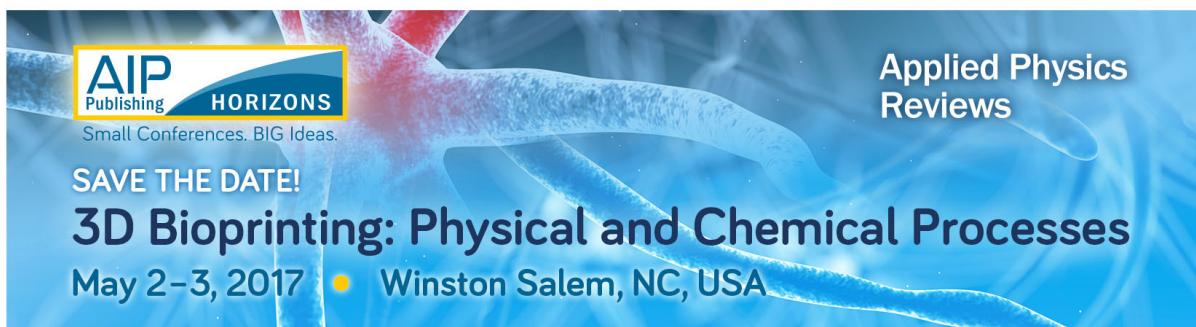
Xiang-Bai ChenJesse Huso, John L. Morrison, and Leah Bergman

Citation: *Journal of Applied Physics* **102**, 116105 (2007); doi: 10.1063/1.2822156

View online: <http://dx.doi.org/10.1063/1.2822156>

View Table of Contents: <http://aip.scitation.org/toc/jap/102/11>

Published by the American Institute of Physics



The properties of ZnO photoluminescence at and above room temperature

Xiang-Bai Chen^{a)}

Department of Physics, Ewha Womans University, Seoul, South Korea

Jesse Huso, John L. Morrison, and Leah Bergman

Department of Physics, University of Idaho, Moscow, Idaho 83844-0903, USA

(Received 18 September 2007; accepted 15 October 2007; published online 11 December 2007)

A study of the photoluminescence characteristics of a ZnO single crystal at the temperature range 173–823 K is presented. The analysis employed the electron-phonon interaction model as well as the radiative recombination rate model. Both studies indicate that at ~ 700 K the photoluminescence character undergoes a transition from being a free exciton emission to a band gap recombination, implying a breakup of excitons into free carriers is occurring. The transition temperature corresponds to ~ 60 meV, which is consistent with the binding energy of the free exciton in ZnO. © 2007 American Institute of Physics. [DOI: 10.1063/1.2822156]

ZnO is a highly ultraviolet (UV) luminescent direct band gap semiconductor with a band gap of ~ 3.37 eV at room temperature.¹ ZnO has a large free exciton binding energy of about 60 meV, which is larger than that of room temperature thermal energy (~ 25 meV). The deep excitonic level results in optical emissions that are thermally stable and significantly efficient at and around room temperature under low excitation energy.^{1,2} The thermal stability of ZnO has advantages in optoelectronic applications such as UV lasing media.³ Optical pumped stimulated emission has been demonstrated in ZnO films^{4,5} and ZnO nanowires.⁶ Also, it has been shown that a low power threshold (2 mW) room temperature polariton laser can be realized with ZnO based microcavities.⁷

The nature of ZnO excitonic emissions at and below room temperature has been extensively investigated.⁸ This research focuses on a study concerning the properties of the photoluminescence (PL) of a ZnO single crystal at the high temperature regime of 173–823 K. We found that 700 K is the onset temperature at which the PL undergoes a transition from being a free exciton emission to a band gap recombination like luminescence. This transition temperature corresponds to an activation energy of ~ 60 meV which is consistent with the values in the literature for the binding energy of the A exciton in ZnO.^{9–11}

Our experiments utilized a JY-Horiba microphotoluminescence/Raman system consisting of a high-resolution T-64000 triple monochromator and an UV microscope capable of focusing a spot size of $\sim 1 \mu\text{m}$ in diameter. A He-Cd Kimmon laser with a wavelength of 325 nm (3.8 eV) was employed as the excitation source. The temperature dependent PL measurements were carried out utilizing an Insteec microcell in the temperature range of 173–823 K. The PL was acquired from the *c* face of a ZnO single crystal in a backscattering geometry, with the polarization of the laser light such that $E \perp c$ (α geometry).

In order to study the nature of the PL at the elevated temperature regime two models were utilized: one is the renormalization of the band gap model as was proposed by Vina *et al.*¹² and the other is the radiative recombination rate model established by Fouquet *et al.*¹³ According to the band gap renormalization model, known also as the electron-phonon interaction, the PL as a function of temperature is expected to be in accordance with the relation^{12,14–17}

$$E_x(T) = E_x(0) - \frac{2\lambda}{\exp(\Theta/T) - 1}. \quad (1)$$

In Eq. (1), $E_x(0)$ is the PL energy at 0 K, λ is a measure of the strength of the electron-average phonon interaction, and Θ corresponds to a mean temperature value of both the longitudinal acoustic and optical phonons taking place in the interaction.^{12,14–16} The average phonon temperature, Θ , is related to the average phonon energy, E_p , via the Boltzmann constant k_B : $\Theta = E_p/k_B$. In Eq. (1), it was assumed that the binding energy of the exciton of ZnO is independent of the temperature; thus the exciton follows the renormalization of the band gap. Figure 1 presents the spectra of the PL at several temperatures and Fig. 2 presents a fit of Eq. (1) to the data. The parameters obtained from the curve fit were found to be $E_x(0) = 3.375$ eV, $\lambda = 0.046$ eV, and $\Theta = 212$ K. These parameters are similar to those that have been previously reported for the free exciton A in ZnO.¹⁸

The key observation in Fig. 2 is that above 700 K the data do not obey the model of Eq. (1); instead the PL energy increases with increasing temperature. This energy increase may represent the breakup of the excitons into free carriers, i.e., an emission which undergoes transition from being excitonic in nature into band gap recombination. In general, when the thermal energy is comparable with that of the binding energy of a free exciton, the excitons are expected to thermalize up into the conduction band, which results in band gap PL emission. As can be seen in Fig. 2, an onset temperature of ~ 700 K is evident, which corresponds to a binding energy of ~ 60 meV. This value of the binding energy is consistent with the values found previously for the binding energy of the free exciton in ZnO.^{9–11} In light of our

^{a)}Author to whom correspondence should be addressed. Electronic mail: xchen@ewha.ac.kr.

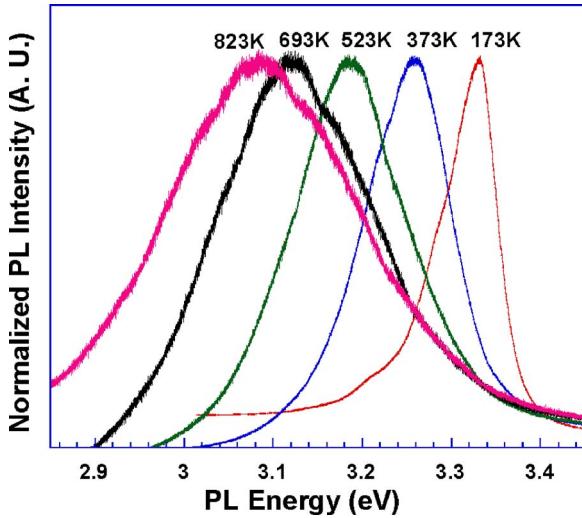


FIG. 1. (Color online) PL spectra of the ZnO single crystallite at various temperatures.

study, we conclude that at the temperature regime $T < 700$ K, the emission is due to free excitons, while at a higher temperature range of approximately 700–823 K, the free excitons start to break up into free carriers. A breakup of excitons into free carriers was previously observed in GaAs multiquantum well structure as well as in GaN thin films.^{13,19}

In order to gain further insight into the characteristics of the PL of ZnO single crystal at the elevated temperature range, we investigated the response of the PL intensity as a function of both the temperature as well as the laser excitation power. Based on the radiative recombination rate model, the PL intensity, I_{PL} , depends on the excitation laser, I_{Laser} , via^{13,20,21}

$$I_{\text{PL}} = \eta I_{\text{Laser}}^{\alpha}. \quad (2)$$

In this relation η is the emission efficiency and the exponent α represents the radiative recombination mechanism. The model predicts that for free exciton recombination $\alpha \approx 1$,

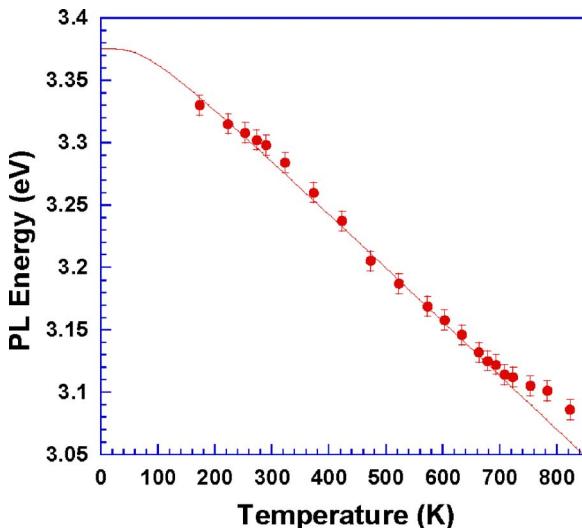


FIG. 2. (Color online) The PL emission energy as a function of temperature. Experimental data (dots) and the fit to the model of Eq. (1) (line) are shown for a temperature range of 173–650 K.

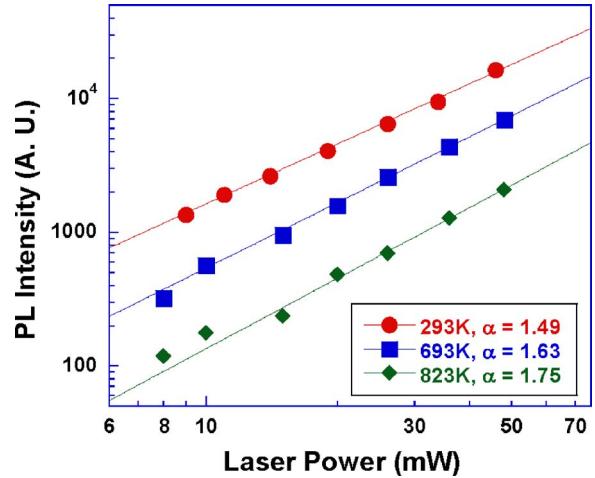


FIG. 3. (Color online) The PL intensity as a function of laser power for several representative temperatures. Experimental data (dots) and the fit to the model of Eq. (2) (lines) are shown.

while for band gap recombination, i.e., free-carrier electron-hole bimolecular recombination, $\alpha \approx 2$. Numerous experimental studies on various semiconductors such as AlAs, GaAs, CdSe, ZnO, and GaN have utilized the theoretical model of Eq. (2) in order to analyze the nature of the photoluminescence properties.^{13,20–30}

In addition to the value of the exponent ascertained utilizing the radiative recombination rate model, one may extract additional knowledge concerning the breakup of excitons into free carriers via the study of the exponent as a function of temperature. Specifically, if there is an emission-type transition from free exciton recombination into band gap emission, an increase of the value α should be observed as a function of temperature. Figure 3 depicts the PL intensity as a function of laser power, as well as the fit to the model of Eq. (2), for several representative temperatures. From the fits presented in Fig. 2, the values of the exponents were found. We repeated that analysis for the entire temperature range of 300–823 K and Fig. 4 presents the temperature dependence of the exponent α . As is depicted in Fig. 4, at

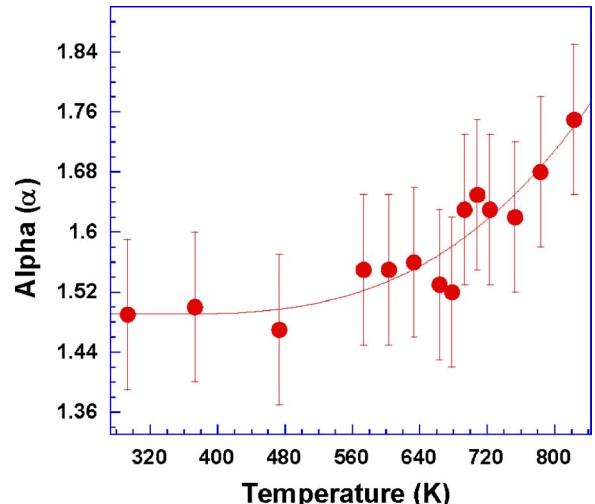


FIG. 4. (Color online) The temperature dependence of the exponent α (the line is not a fit).

temperatures below ~ 700 K, the exponent has approximately a constant value of ~ 1.5 , while above 700 K, α becomes an increasing function of the temperature. In accordance with the radiative recombination rate model, the PL of the ZnO single crystal is governed mainly by excitonic emission at the low temperature regime ($T < 700$ K), while at the elevated temperature range an onset into free carrier recombination takes place as is implied via the increasing value of α . The onset temperature ~ 700 K is consistent with that found via the electron-phonon model approach (see Fig. 2). As can be seen in Fig. 4, at $T > 700$ K, the exponent is slowly approaching the value 2 which implies that the PL has a mixed character of band gap as well as exciton emissions.

In conclusion, we investigated the light emission characteristics of a ZnO single crystal at the temperature range 173–823 K. The analysis employed the electron-phonon interaction model as well as the radiative recombination rate model. Both studies indicate that at ~ 700 K, the PL emission undergoes a transition from being a free exciton emission to a band gap recombination. The transition temperature corresponds to ~ 60 meV, which is consistent with the binding energy of the free exciton in ZnO.

ACKNOWLEDGMENTS

The authors gratefully acknowledge NSF CAREER DMR-0238845 and DOE-DE-FG02-04ER46142, as well as the American Chemical Society PRF 40749-AC10.

¹Y. F. Chen, D. M. Bagnall, H. Koh, K. Park, K. Hiraga, Z. Zhu, and T. Yao, *J. Appl. Phys.* **84**, 3912 (1998).

²A. Ohtomo, M. Kawasaki, Y. Sakurai, I. Ohkubo, R. Shiroki, Y. Yoshida, T. Yasuda, Y. Segawa, and H. Koinuma, *Mater. Sci. Eng., B* **56**, 263 (1998).

³Q. X. Zhao, M. Willander, R. E. Morjan, Q.-H. Hu, and E. E. B. Campbell, *Appl. Phys. Lett.* **83**, 165 (2003).

⁴P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasakki, A. Ohtomo, H. Koinuma, and Y. Segawa, *Solid State Commun.* **103**, 459 (1997).

⁵D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, *Appl. Phys. Lett.* **70**, 2230 (1997).

⁶M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* **292**, 1897 (2001).

⁷M. Zamfirescu, A. Kavokin, B. Gil, G. Malpuech, and M. Kaliteevski, *Phys. Rev. B* **65**, 161205 (2002).

⁸B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straburg, M. Dworzak, and U. Haboeck, *Phys. Status Solidi B* **241**, 231 (2004).

⁹W. Y. Liang and A. D. Yoffe, *Phys. Rev. Lett.* **20**, 59 (1968).

¹⁰D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, *Phys. Rev. B* **60**, 2340 (1999).

¹¹X. D. Wang, C. J. Summers, and Z. L. Wang, *Nano Lett.* **4**, 423 (2004).

¹²L. Viña, S. Logothetidis, and M. Cardona, *Phys. Rev. B* **30**, 1979 (1984).

¹³J. E. Fouquet and A. E. Siegman, *Appl. Phys. Lett.* **46**, 280 (1985).

¹⁴P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, *Phys. Rev. B* **35**, 9174 (1987).

¹⁵A. Manoogian and A. Leclerc, *Phys. Status Solidi B* **92**, K23 (1979).

¹⁶A. Manoogian and J. C. Woolley, *Can. J. Phys.* **62**, 285 (1983).

¹⁷L. Bergman, M. Dutta, M. A. Stroscio, S. M. Komirenko, R. J. Nemanich, C. J. Eiting, D. J. H. Lambert, H. K. Kwon, and R. D. Dupuis, *Appl. Phys. Lett.* **76**, 1969 (2000).

¹⁸H. P. He, Z. Z. Ye, S. S. Lin, H. P. Tang, Y. Z. Zhang, L. P. Zhu, J. Y. Huang, and B. H. Zhao, *J. Appl. Phys.* **102**, 013511 (2007).

¹⁹X. B. Chen, J. Huso, J. L. Morrison, and L. Bergman, *J. Appl. Phys.* **99**, 046105 (2006).

²⁰S. Jin, Y. Zheng, and A. Li, *J. Appl. Phys.* **82**, 3870 (1997).

²¹H. P. Zhou and C. M. S. Torres, *J. Appl. Phys.* **75**, 3571 (1994).

²²Z. Y. Xu, J. Z. Xu, W. K. Ge, B. Z. Zheng, J. Y. Xu, and Y. Z. Li, *Solid State Commun.* **61**, 707 (1987).

²³T. Schmidt, K. Lischka, and W. Zulehner, *Phys. Rev. B* **45**, 8989 (1992).

²⁴T. Taguchi, J. Shirafuji, and Y. Inuishi, *Phys. Status Solidi B* **68**, 727 (1975).

²⁵D. E. Cooper, J. Bajaj, and P. R. Newmann, *J. Cryst. Growth* **86**, 544 (1990).

²⁶Z. C. Feng, A. Mascarenhas, and W. J. Choyke, *J. Lumin.* **35**, 329 (1986).

²⁷D. L. Rosen, Q. X. Li, and R. R. Alfano, *Phys. Rev. B* **31**, 2396 (1985).

²⁸H. C. Ko, D. C. Park, Y. Kawakami, S. Fujita, and S. Fujita, *Appl. Phys. Lett.* **70**, 3278 (1997).

²⁹K. Domen, A. Kuramata, and T. Tanahashi, *Appl. Phys. Lett.* **72**, 1359 (1998).

³⁰L. Bergman, X. B. Chen, J. L. Morrison, J. Huso, and A. P. Purdy, *J. Appl. Phys.* **96**, 675 (2004).