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Photoluminescence study of ZnO nanotubes under hydrostatic pressure

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Photoluminescence of ZnO single crystal nanotubes grown on sapphire substrate by metal organic chemical vapor deposition has been studied as a function of applied hydrostatic pressure using the diamond-anvil-cell technique. The photoluminescence spectra of the ZnO nanotubes at atmospheric pressure are dominated by strong near-band-edge Γ_{FX} and Γ_{BX} excitonic emission lines accompanied by a weak broad deep-level (DL) emission band. The pressure-induced shifts of all observed emission lines are followed up to 15 Gpa, when ZnO nanotubes undergo a phase transition from a direct-gap wurtzite structure to an indirect-gap rocksalt structure. The Γ_{FX} emission is found to shift toward higher energy with applied pressure at a rate of 29.6 meV/GPa, which provides a method to measure the pressure coefficient of the direct Γ band gap in the wurtzite ZnO nanotubes. The Γ_{BX} emission has a pressure coefficient of 21.6 meV/GPa, about 30% smaller than that of the ZnO band gap, which suggests that it might originate from the radiative recombination of the excitons bound to donorlike deep centers rather than shallow donors. The pressure coefficient of the broad DL emission band in ZnO tube is 16.8 meV/GPa, which indicates that the initial states involved in the emission process are deep localized states. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2191884]

Semiconductor nanostructures have been attracting increasing attention due to their exceptional properties different from bulk materials. Among the wide variety of semiconductor nanostructures, ZnO nanostructures, as a wide-band-gap semiconductor, are even more attractive for high-efficiency short-wavelength optoelectronic nanodevices, due to their large excitonic binding energy (~60 meV) and high mechanical and thermal stabilities.[1–3] Recently, various ZnO low-dimensional nanostructures, such as nanodots,[4] nanorods,[5] nanobelts and nanoribons,[6] nanosheets,[7] and nanotubes,[8–10] along with their optical properties have been reported. As for nanoscale tubular structures, there have been stimulated intensive research interests because of their exceptional physical properties,[11,12] i.e., ballistic transport or Luttinger liquid behavior in the molecular regime,[13] and potential applications in constructing nanoscale devices.[14]

Though the electronic and optical properties of the ZnO bulk, films and nanostructures have been widely studied,[15–17] the successful development of advanced optoelectronic devices will likely require a better understanding of the defect formation and recombination processes in ZnO. The pressure dependence of photoluminescence (PL) emission yields valuable information on the electronic band structure and optical properties. Unfortunately, there have been not many reported works about this issue to the best of our knowledge, expect that Shan *et al.* recently reported their results of a pressure-dependent study on the optical properties of ZnO nanowires.[18] Apparently more detailed experimental and theoretical works are needed to fully understand the electronic energy band structure and the structural properties of ZnO. Here, we present PL measurements of wurtzite ZnO nanotubes under high pressure up to 15 GPa. The essential features of the PL spectra and their behavior under pressure are investigated. The pressure coefficients of all the features observed in ZnO nanotubes are discussed.

The ZnO nanotubes used in this study was grown on sapphire substrates by metal organic chemical vapor deposition.[19] Typical scanning electron microscopy (SEM) image of the tubes is shown in Fig. 1. It is seen that the tube has hexagonal shape. The length of the tube was up to several microns. The wall thickness of the tube is about 100 nm. The well-defined hexagonal shape is an indication of epitaxial growth and consequently single crystal nature of the tubes.

Photoluminescence measurements under applied hydrostatic pressure were performed at room temperature. The 325 nm line of a He–Cd laser was used as excitation source.

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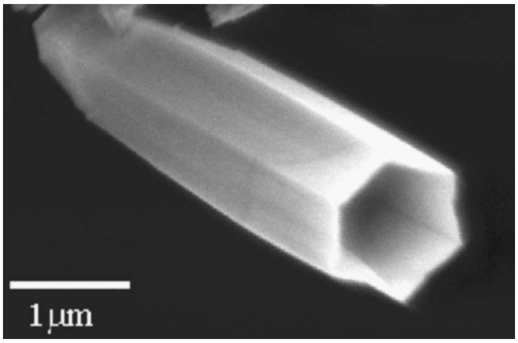

FIG. 1. SEM image of ZnO nanotube prepared by metal organic chemical vapor deposition.

The PL signals were collected by a JY HR800 spectrometer equipped with a charge coupled device (CCD) detector. ZnO nanotubes was carefully removed from the substrate and loaded into a gasketed diamond anvil cells (DAC). The pressure medium is a 4:1 methanol/ethanol mixture. The applied pressure was determined by a standard method of monitoring the shift of the ruby R1 line.

PL spectra of the ZnO nanotubes for a few selected pressures are shown in Fig. 2. The PL spectrum taken at atmospheric pressure exhibits the dominant near-band-edge exciton transitions and a broadband deep-level (DL) emission structure centered in the yellow spectral region. Zoom-in spectrum illustrates that the dominant near-band-edge exciton transitions consist of two emission lines. Temperature dependent PL measurements suggest that the emission line at 3.24 eV (Γ_{BX}) can be attributed to the radiative recombination of bound exciton and the one at 3.28 eV (Γ_{FX}) can be assigned to intrinsic free-exciton emission.[17] Under applied pressure, these excitonic spectral features and the DL emission were found to shift towards higher energy as the ZnO band gap increases. The intensity of the DL emission band relative to that of the Γ_{FX} emission was found to decrease with pressure. The near-band-edge PL features did not decrease in intensity until the applied pressure approached 11 GPa. At the pressure above 11 GPa, the PL intensity decreased rapidly and was completely quenched at 11–15 GPa, under which the samples were undergoing pressure-induced phase transition from a direct-gap wurtzite to an indirect-gap rocksalt structure.[20,21] The PL does not recover at atmospheric pressure once the sample has undergone the phase transition. The lack of PL and a clearly visible change in sample color from white to light yellow suggest that the ZnO tube retains the rocksalt phase at ambient pressure. Another weak broadband luminescence with multipeak structures in the blue-green spectral region was also observed, which should be attributed to the fluorescence of the diamond anvils under the excitation of the 325 nm laser line.[22]

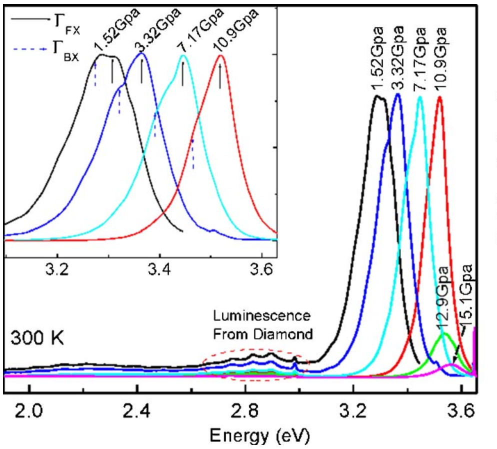

FIG. 2. (Color online) PL spectra from ZnO nanotubes for selected pressures consist of two excitons emissions and a very broad yellow emission band.

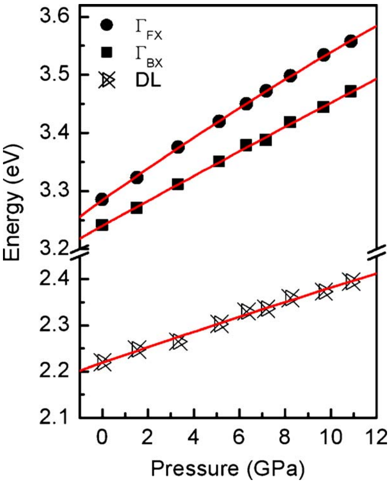

FIG. 3. (Color online) Dependence of the energy positions on pressure for the various observed emissions in ZnO nanotubes sample. The solid line represents the result of the best quadratic fitting.

Figure 3 shows the variations of the energy positions of all observed emission lines as a function of applied pressure. The energy positions of the DL emission band are obtained by fitting the spectral curves to a Gaussian profile. The solid lines represent the results of least-squares fits to the experimental data using a quadratic equation. The fitted results for the Γ_{FX}, Γ_{BX}, and DL emission band are listed in Table I. It can be seen that the pressure dependence of the Γ_{FX} emission line observed in ZnO nanotubes is 29.6 meV/GPa; this value is comparable with that of ZnO nanowires (29.2 meV/GPa) and our previous result (29.7 meV/GPa) from ZnO nanosheets using PL measurements under applied pressures.[18,23] The pressure coefficient of the Γ_{FX} emission can be approximately regarded as a signature of the direct Γ band-gap dependence on applied pressure for wurtzite ZnO nanotubes. This is because the electronic states involved in the radiative recombination processes of free excitons or shallow bound excitons can be described within the framework of the effective-mass approximation and are expected to closely follow their respective band edges.[24]

It should be noted that the pressure coefficient of Γ_{BX} is only 21.6 meV/GPa, almost 30% smaller than that of the Γ_{FX}. Application of pressure increases the binding energy of a shallow exciton arising from an increase of electron effective mass and a decrease in dielectric constant as the band

TABLE I. Pressure coefficients of various observed emissions observed in the ZnO nanotubes studied in this work.

	$E(P=0)$ (eV)	dE/dP (meV/GPa)	d^2E/dP^2 (meV/GPa^2)
Free exciton (Γ_{FX})	3.2807	29.6	−0.14
Bound exciton (Γ_{BX})	3.2241	21.6	−0.22
DL emission band	2.2159	16.8	−0.15

gap increases.[25,26] The pressure-induced increase in exciton binding in ZnO has been estimated to vary the pressure coefficient of Γ_{BX} by less than 1% in numerical value. Therefore the effect of pressure on the binding energy is not likely to produce a significant difference between the pressure coefficient of Γ_{BX} and that of the ZnO band gap. The pressure dependence of the Γ_{BX} line is expected to be ZnO-like ($dE/dp=29.6$ meV/GPa) if it originates from the recombination of the excitons bound to shallow donors described on the basis of the effective-mass approximation. The recombination line associated with the radiative decay of an exciton bound to a neutral or ionized donor should shift with the host semiconductor band gap under hydrostatic pressure at almost the same rate, since the bound electron stays in the orbit of shallow donor states associated with the conduction-band edge and the excitonic hole bound in the Coulomb field retains the symmetry of the valence-band edges. However, the effect of pressure on the Γ_{BX} emission line obtained in this work ($dE/dP=21.6$ meV/GPa) shows an inconsistency with the shallow donor-bound exciton model. It suggests that Γ_{BX} might result from the radiative recombination of the excitons bound to donorlike deep centers rather than shallow donors according to our results, because the pressure dependence of an energy level of a deep center is mainly determined by the composition of its wave function and the pressure coefficient of a deep donor will be determined mainly by the pressure dependence of the average conduction band energy.[27]

The broadband DL emission spectral structure could be commonly observed in the PL spectral of ZnO single crystals and nanostructures. The DL emission band of our ZnO nanotubes shifts at a rate of 16.8 meV/GPa, much smaller than that of the ZnO band gap. The difference is not surprising, since the DL luminescence is associated with deep localized defects such as structural defects, single ionized vacancies, and impurities.[28,29] Even though the energy levels of the free excitons and shallow impurities follow the band edge closely, the deep localized defects need not follow the band edge. The difference between the shift of the DL luminescence level and band edge can be attributed to the shift of the deep localized defects level with respect to the valence band.

In conclusion, pressure-dependent photoluminescence measurements have been performed at room temperature on the single crystal ZnO nanotubes for the first time. The pressure induced energy shift of the free exciton emission in the sample allows us to determine the pressure coefficient for the fundamental band gap of the ZnO nanotubes to be 29.6 meV/GPa. The smaller pressure coefficient of 21.6 meV/GPa suggests that the Γ_{BX} emission originates from the radiative recombination of the excitons bound to donorlike deep centers rather than the shallow donors. The broad DL emission band in ZnO tube depends on pressure with a linear slope of 16.8 meV/GPa. It indicates that the initial states involved in the emission process are deep localized states.

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[1] S. C. Jain, M. Willander, J. Narayan, and R. Van Overstraeten, J. Appl. Phys. **87**, 965 (2000).
[2] C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H. Lee, Appl. Phys. Lett. **81**, 3648 (2002).
[3] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).
[4] S. W. Kim, S. Fujita, and S. Fujita, Appl. Phys. Lett. **81**, 5036 (2002).
[5] J. J. Wu and S. C. Liu, Adv. Mater. (Weinheim, Ger.) **14**, 215 (2002).
[6] Z. W. Pan, Z. R. Dai, and Z. L. Wang, Science **291**, 1947 (2001).
[7] S. J. Chen, Y. C. Liu, C. L. Shao, R. Mu, Y. M. Lu, J. Y. Zhang, D. Z. Shen, and X. W. Fan, Adv. Mater. (Weinheim, Ger.) **17**, 586 (2005).
[8] J. J. Wu, S. C. Liu, C. T. Wu, K. H. Chen, and L. C. Chen, Appl. Phys. Lett. **81**, 1312 (2001).
[9] J. Hu, Y. Bando, and Z. Liu, Adv. Mater. (Weinheim, Ger.) **15**, 1000 (2003).
[10] R. M. Wang, Y. J. Xing, J. Xu, and D. P. Yu, New J. Phys. **5**, 115 (2003).
[11] S. Iijima, Nature (London) **354**, 56 (1991).
[12] C. Lieber and P. Yang, Nature (London) **319**, 553 (2002).
[13] Z. Yao, H. W. Ch. Postma, L. Balents, and C. Dekker, Nature (London) **402**, 273 (1999).
[14] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science **294**, 1317 (2001).
[15] C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H. Lee, Appl. Phys. Lett. **81**, 3648 (2002).
[16] J. Zhang, W. Yu, and L. Zhang, Phys. Lett. A **299**, 276 (2002).
[17] S. J. Chen, Y. C. Liu, J. Y. Zhang, Y. M. Lu, D. Z. Shen, and X. W. Fan, J. Phys.: Condens. Matter **15**, 1975 (2003).
[18] W. Shan, W. Walukiewicz, J. W. Ager III, K. M. Yu, Y. Zhang, S. S. Mao, R. Kling, C. Kirchner, and A. Waag, Appl. Phys. Lett. **86**, 153117 (2005).
[19] B. P. Zhang, N. T. Binh, K. Wakatsuki, Y. Segawa, Y. Yamada, N. Usami, M. Kawasaki, and H. Koinuma, Appl. Phys. Lett. **84**, 4098 (2004).
[20] S. Desgreniers, Phys. Rev. B **58**, 14102 (1998).
[21] J. Z. Jiang, J. S. Oslen, L. Gerward, D. Frost, D. Rubie, and J. Peyronneau, Europhys. Lett. **50**, 48 (2000).
[22] P. J. Dean, Phys. Rev. **139**, A588 (1965).
[23] S. J. Chen, Y. C. Liu, C. L. Shao, C. S. Xu, Y. X. Liu, L. Wang, B. B. Liu, and G. T. Zou, J. Appl. Phys. **98**, 106106 (2005).
[24] S. Lai and M. V. Klein, Phys. Rev. Lett. **44**, 1087 (1980).
[25] D. J. Wolford and J. A. Bradley, Solid State Commun. **53**, 1069 (1985).
[26] G. A. Samara, Phys. Rev. B **27**, 3494 (1983).
[27] J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
[28] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).
[29] J.-J. Wu and S.-C. Liu, Adv. Mater. (Weinheim, Ger.) **14**, 215 (2002).