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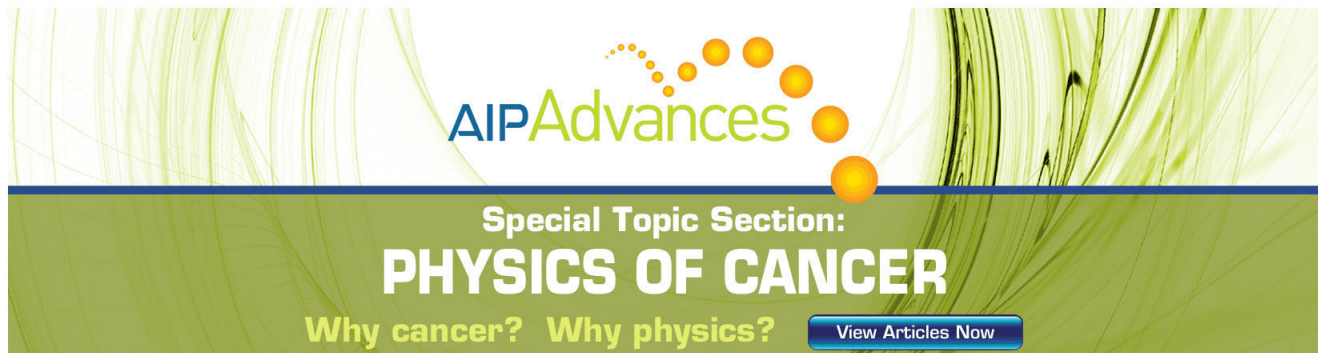
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Photoluminescence of wurtzite ZnO under hydrostatic pressure

S. J. Chen

*Centre for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, People's Republic of China
and Key Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 East-South Lake Avenue, Changchun 130033, People's Republic of China*

Y. C. Liu,^{a)} C. L. Shao, C. S. Xu, and Y. X. Liu

Centre for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, People's Republic of China

L. Wang, B. B. Liu, and G. T. Zou

National Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

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Photoluminescence (PL) spectra of single-crystal ZnO bulk under hydrostatic pressure are studied using the diamond-anvil-cell technique at room temperature. The PL spectrum of ZnO single crystal taken at atmospheric pressure was dominated by a strong near-band-edge exciton emission. The emission line was found to shift towards higher energy with increasing applied pressure. By examining the pressure-dependent PL spectral features, the pressure coefficient of the direct Γ band gap of the wurtzite ZnO was determined. The hydrostatic deformation potential of the band gap has also been deduced from the experimental results. © 2006 American Institute of Physics.
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The ZnO is a wide-band-gap *n*-type semiconductor, with a direct band gap energy of 3.37 eV and an excitation banding energy of 60 meV.¹ The near-band-edge emission, transparent conductivity, and piezoelectricity make ZnO become one of the most important functional semiconductor oxides, serving to the field emitters, optoelectronic devices and sensors, etc. The outstanding thermal and chemical stabilities also allow the ZnO-based electronic and optoelectronic devices to operate at high temperatures and in hostile environments. Recently, there have been many studies on the electronic and optical properties of the ZnO bulk, films, and nanostructures.^{2–6} In particular, the pressure dependence of the photoluminescence (PL) is very useful in understanding the energy band structure and the structural properties of semiconductors, such as GaN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$.^{7,8} However, the pressure dependence of the optical transitions in ZnO, which can provide important insight into the nature of radiative decay processes of photoexcited carriers, have seldom been explored. There have been only several reported studies of the pressure dependence of the band edge in ZnO with absorption,^{9,10} reflection,¹¹ and two-photon absorption.¹² This fact limits the understanding of the electronic energy band structure and the structural properties, which are of importance in the development of high quality optoelectronic devices. Furthermore, nanosized materials often have physical and chemical properties under applied pressure, differing from those of the corresponding bulk materials. The issue of the effects of the applied pressure on the electronic energy band structure and the structural properties in the ZnO bulk

material is of considerable interest from a fundamental viewpoint, and also with respect to providing a convincing reference to probe the ZnO nanomaterials behavior under applied pressure. In this work, we present the results of a study of the pressure effect on the structural and optical properties of ZnO single crystal using Raman and PL spectroscopies.

The ZnO sample used in this study is a ZnO single crystal grown by MTI Corp. using hydrothermal method. The PL was excited by the 325 nm line (3.81 eV) of a He–Cd laser, and was collected in “backscattering” configuration by a JY HR800 spectrometer with a charge coupled device (CCD) detector. Application of hydrostatic pressure was accomplished by mounting small sample chips with sizes of $\sim 200 \times 200 \mu\text{m}^2$ into the 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. In order to identify the phase transition of ZnO, *in situ* Raman spectra were measured with varying pressure. The 488 nm line of an Ar^+ -ion laser with a power of 17 mW on the diamond surface was used for Raman scattering and ruby luminescence measurements.

Figure 1 shows the Raman spectra which were recorded at selected pressures at room temperature with increasing and decreasing pressures. All observed spectral peaks taken at atmospheric pressure can be signed to a wurtzite ZnO structure according to the literature values.¹³ Under hydrostatic pressure, all the Raman-scattering peaks shift to higher frequency with increasing pressures. A clear wurtzite to rock salt transition is observed starting at 8.3 GPa and completing at 9 GPa with increasing pressure. The high pressure rock-salt phase is stable up to 30 GPa, the highest pressure

^{a)}Author to whom correspondence should be addressed; electronic mail: ycliu@nenu.edu.cn

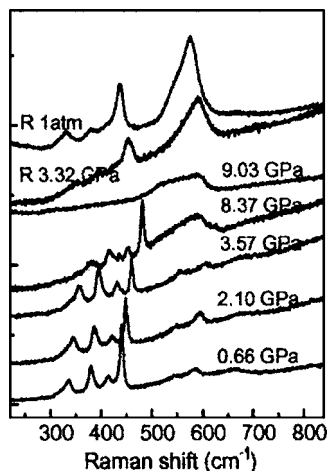


FIG. 1. *In situ* high-pressure Raman spectra at room temperature with increasing and decreasing pressures for ZnO single crystal.

achieved in the present study. Upon decompression, the rock-salt structure is maintained beyond the upstroke transition pressure: the ZnO single crystal reverts to the wurtzite structure at about 3 GPa, below which a single phase is present. The phase hysteresis is consequently substantial. The transition pressure is in good agreement with the previously reported values in the case of bulk ZnO,^{14–16} which are listed in Table I.

Figure 2 shows typical PL spectra of the ZnO sheets at atmospheric pressure and at several selected higher pressure values. The PL spectrum taken at atmospheric pressure from the ZnO nanosheets exhibits a single UV peak located at about 3.30 eV due to near-band-edge (NBE) exciton transitions. Under applied pressure, the NBE emission line shifts towards higher energy, implying an increase of the direct band gap. The PL spectral feature does not broaden significantly and decrease in intensity drastically with increasing pressure. At pressures above 8.6 GPa, the PL signal disappears as a result of the pressure-induced phase transition from the wurtzite to rock-salt structure, the later is predicted to be an indirect narrow gap semiconductor.¹⁷ This is because *p* and *d* states mix away from the Γ point and resulting *p*-*d* repulsion results in the upwards dispersion of *p* bands in directions Γ -*K*(Σ) and Γ -*L*(Λ) of the Brillouin zone, which, consequently, make the valence band maxima occur away from the Γ point and the material has indirect character. The optically determined phase transition pressure is observed to correlate extremely well with the structural phase transition pressure determined by high pressure Raman scattering. The

TABLE I. Transition pressures and pressure coefficients for the fundamental band gap of wurtzite ZnO.

Transition pressure, <i>P</i> (GPa)	8.6±0.3 ^a	9.1±0.2 ^b	8.7 ^c	8.57 ^d
$\alpha = dE/dP$ (meV/GPa)	23.5±0.8 ^a	24.5±0.8 ^c	25.6±2 ^f	29.7 ^g

^aThis work.

^bReference 14.

^cReference 15.

^dReference 16.

^eReference 9.

^fReference 12.

^gReference 18.

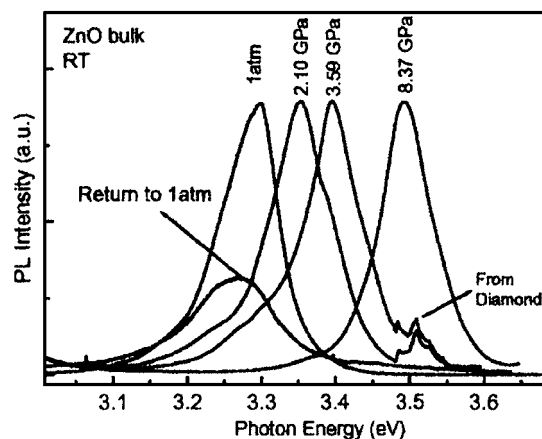


FIG. 2. NBE luminescence spectra of ZnO single crystal measured at RT for selected pressures.

NBE emission is recovered as the pressure is released. This result is in good agreement with the complete recovery of the hexagonal phase observed in Raman scattering. However, significant decrease in intensity, some redshift and broadening of the recovered NBE emission line upon release of pressure are observed, which could be due to an elevated number of structure defects, formed through the rearrangement of the structure with multiple transitions at room temperature.

The pressure-induced energy shift of the NBE emission is plotted in Fig. 3. The solid line in Fig. 3 is the least-square fit to the experimental data using a linear pressure dependent fit function,

$$E(P) = E(0) + \alpha P, \quad (1)$$

where the energy *E* is in eV and the pressure *P* is in GPa. The best fit to the data yields the pressure coefficient $\alpha = 23.5 \pm 0.8 \times 10^{-3}$ eV/GPa. The pressure coefficient derived from the experimental data and the previously reported values^{9,12,18} are listed in Table I.

It is known that the emission lines associated with the radiative decay of a free exciton or a shallow bound exciton shifts with the host semiconductor band gap under hydrostatic pressure at the same rate. The electron stays in the conduction-band edge states or in the orbit of shallow donor states associated with the conduction-band edge and the ex-

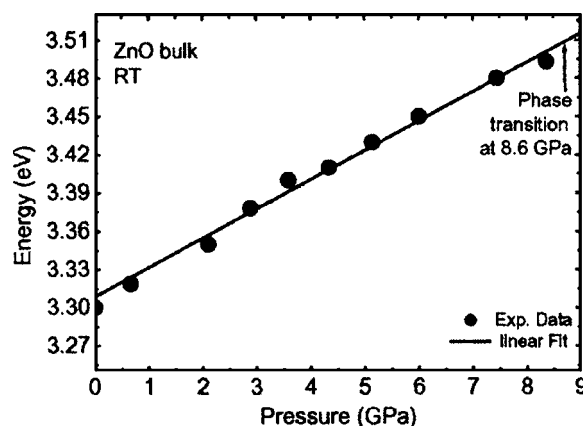


FIG. 3. Change of the band gap energy of ZnO with pressure. The solid line is the best linear of the data.

citonic hole bound in the Coulomb field retains the symmetry of the valence-band edges. Therefore, the change of the intense and sharp NBE transition with pressure was plotted in the Fig. 3 to provide a direct signature of the pressure-dependent direct Γ band gap for wurtzite ZnO.

The application of hydrostatic pressure, inducing a shift of the conduction-band edge relative to the valence-band edge due to a change in the volume, allows a direct estimation of the hydrostatic deformation potential for the direct Γ band gap of the wurtzite ZnO. This is because the *effective* hydrostatic deformation potential is isotropic stress induced from hydrostatic pressure. The deformation potential is defined as $\alpha = \partial E / \partial \ln V$. In terms of relative volume change, the variation of the band gap with pressure can also be appropriately expressed as:

$$\Delta E = \alpha[(V - V_0)/V] + \gamma[(V - V_0)/V]^2, \quad (2)$$

where α is the hydrostatic deformation potential for the Γ band gap, and γ the quadratic dependence of the band gap on the relative volume change. The relative volume change caused by the applied pressure can be related by the Murnaghan equation of state:¹⁹

$$P = (B_0/B'_0)[(V_0/V)^{B'_0} - 1], \quad (3)$$

where B_0 is the bulk modulus of the wurtzite ZnO and B'_0 is its pressure derivative ($=dB/dP$). By fitting the experimental data to Eq. (3), using recently reported values of $B_0 = 183$ GPa and $B'_0 = 4$,¹⁵ the deduced hydrostatic deformation potentials for the direct Γ band gap of wurtzite ZnO were found to be $\alpha = -5.15 \pm 0.24$ eV and $\gamma = 14.9 \pm 6$ eV. It should be pointed out that the value of the deformation potential deduced here from fitting experimental data depends on the numerical values of the bulk modulus and its pressure derivative. For instance, the values could be $\alpha = -4.47 \pm 0.2$ eV and $\gamma = 10.0 \pm 4.7$ eV if the alternative values $B_0 = 160$ GPa and $B'_0 = 4.4$ (Ref. 15) obtained by linearized-augmented plane-wave (LAPW) calculations were used. Our deduced deformation potential was comparable with the value from the work reported by Mang *et al.*, with two-photon absorption,¹² in which a hydrostatic deformation potential between -3.51 and -3.81 eV was reported.

In summary, we have studied the photoluminescence of the single-crystal wurtzite ZnO as a function of pressure. The

PL spectrum measured at atmospheric pressure consists of an intense NBE luminescence emission and a very weak DL emission. All PL spectra shift to higher energy with increasing applied pressure and the pressure coefficient has been determined. The pressure coefficient of the NBE transition obtained in this work can be used to describe the pressure dependence of the fundamental band gap of the wurtzite ZnO based on the effective-mass approximation. Our results yield the variation of the Γ band gap with pressure to be $\alpha = 23.5 \pm 0.8 \times 10^{-3}$ eV/GPa and the value of the deformation potential to be $\alpha = -5.15 \pm 0.24$ eV.

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