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Pressure-dependent photoluminescence of ZnO nanosheets

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Photoluminescence and Raman spectra of ZnO single-crystal nanosheets have been studied as a function of applied hydrostatic pressure using the diamond-anvil-cell technique at room temperature. The ZnO nanosheets synthesized via a vapor transport process have uniform plane surfaces with lateral dimensions up to several microns and thickness of ~100 nm. In terms of Raman results, the ZnO nanosheets underwent a transition from wurtzite to rock-salt structure with an increase of pressure, and the phase-transition pressure was measured to be about 11.2 GPa. However, a strong near-band-edge UV emission of ZnO nanosheets was observed with the applied pressure up to 20.0 GPa. Simultaneously, the emission peak shifted to higher-energy side with increasing pressure. By examining the dependence of the near-band-edge emission peak on the applied pressure, the pressure coefficient of the direct Γ band gap in the wurtzite ZnO nanosheets was determined. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2132519]

ZnO is currently attracting increasing attention because of its electronic properties, i.e., a semiconducting band gap of about 3.3 eV and a large exciton binding energy of 60 meV, and the possibilities for application in optoelectronic devices, directly or as a substrate for growth of other semiconductors such as GaN and SiC.[1–4] Contrarily to other II-VI binary compounds which adopt different metastable structures, the equilibrium structure of ZnO at ambient is only a hexagonal wurtzite one (*W*-ZnO) with space group $P6_3/mmc$ (C_{6V}^4) and a fourfold ion coordination. As pressure is raised from an ambient condition, this phase transforms to the cubic rock-salt structure (RS-ZnO) at a pressure in the vicinity of 9 GPa.[5,6] The outstanding thermal and chemical stability of the wide-band-gap ZnO allows its based electronic and optoelectronic devices to operate at high temperatures and in hostile environments. Recently, there have been many studies on the optical properties of the ZnO films and nanostructures.[7–11] In particular, ZnO nanosheets have exhibited surprisingly strong photon emission at temperature as high as 857 K.[12] This finding demonstrates that ZnO nanostructure has the potential for high-temperature optoelectronic applications. However, experimental investigations of 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,[13,14] reflection,[15] and two-photon absorption.[16] This fact poses an obstacle to our understanding of the electronic energy band structure and the structural properties, which are of importance in the development of high quality optoelectronic devices. Furthermore, the pressure dependence of the photoluminescence (PL) is very useful in understanding the energy-band structure and the structural properties of ZnO.

In this investigation, the pressure-induced phase-transition properties of wurtzite ZnO nanosheets are studied by using pressure-dependent Raman scattering up to 30 GPa. The pressure coefficient for the near-band-edge (NBE) emission line was also measured, which provides a direct measure of the pressure coefficient of wurtzite ZnO direct Γ band gap.

The ZnO single-crystal nanosheets used in this study are grown by a vapor transport process. The preparation procedure was reported elsewhere.[12] Typical field-emission scanning electron microscope (FESEM) [Fig. 1(a)] and transmis-

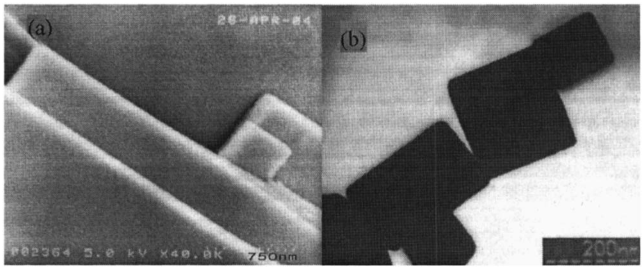

FIG. 1. FESEM and TEM image of ZnO nanosheets.

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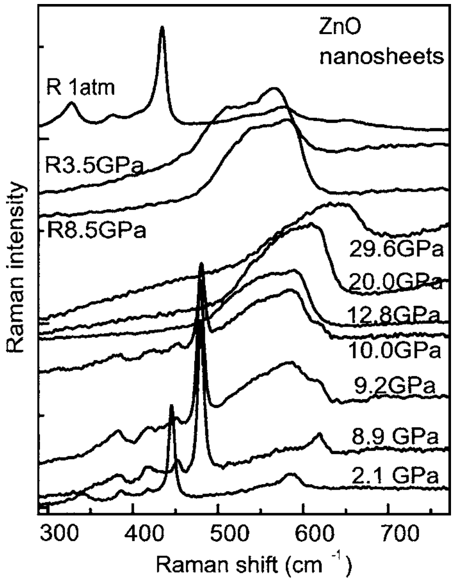

FIG. 2. *In situ* high-pressure Raman spectra at room temperature with increasing and decreasing pressures for ZnO nanosheets. A clear wurtzite-to-rock-salt transition is observed starting at 9.2 GPa and completing at 11.2 GPa. Upon decompression, ZnO nanosheets revert to the wurtzite structure at about 2 GPa.

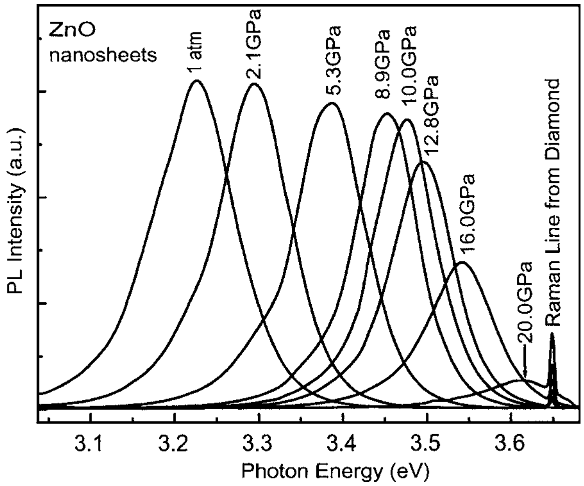

FIG. 3. PL spectra of ZnO nanosheets measured at 300 K for selected pressures.

sion electron microscope (TEM) images [Fig. 1(b)] show that the nanosheets have uniform plane surfaces with lateral dimensions up to several microns and a thickness of 100 nm. X-ray diffraction and Raman-scattering results show that the sheets possess a hexagonal wurtzite structure.

The high-pressure cell was a membrane diamond anvil cell (DAC). A mixture of 4:1 methanol-ethanol was used as pressure-transmitting medium. The applied pressures were determined by monitoring the shift of the ruby *R*1 line. The 488 nm line of an $\mathrm{Ar^+}$-ion laser with a power of 17 mW on the diamond surface was used for Raman scattering and for ruby luminescence measurement. A He–Cd laser at 325 nm with a power of 30 mW on the diamond surface was used for PL excitation.

While the effect of pressure on Raman spectra of ZnO is an interesting issue, similar studies was reported by Decremps *et al.*[17] It is not the focus of this paper, and will be discussed elsewhere in detail. Here, Raman spectra are used simply to identify the phase transition with varying pressure. A large number of Raman spectra were recorded at pressures ranging from 0 to 30 GPa at room temperature with increasing and decreasing pressures. We observed that, all observed spectral peaks taken at atmospheric pressure can be signed to a wurzite ZnO structure according to the literature values,[18] which were listed elsewhere.[12] 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 9.2 GPa and completing at 11.2 GPa with increasing pressure. The two phases coexist over a pressure range of 9.2–11.2 GPa, as shown in Fig. 2. The high-pressure rock-salt phase is stable up to 30 GPa, the highest pressure achieved in the present study. Upon decompression, the rock-salt structure is maintained beyond the upstroke transition pressure: ZnO nanosheets revert to the wurtzite structure at about 2 GPa, below which a single phase is present. The phase hysteresis is consequently substantial. Normally, the transition pressure is 8–9 GPa in the case of bulk ZnO.[5,6] In our case of nanosized ZnO sheets, the phase transformation pressure was increased to 11.2 GPa. Jiang *et al.* believed that the enhancement of transition pressure in ZnO nanocrystal is caused by the surface energy difference between the phases involved.[19]

Figure 3 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 ZnO nanosheets exhibits a single UV peak located at about 3.20 eV due to NBE exciton transitions. The visible emission, commonly observed in ZnO nanostructures,[20–23] was hardly observed compared with the NBE emission, indicating an undetectable concentration of structural defects present.[12] Under hydrostatic pressure, the peak of the PL spectrum shifts toward higher energy as the applied pressure increases. The PL spectral feature does not broaden significantly nor decrease in intensity drastically with increasing pressure from 0 to 11 GPa. At the pressure above 11 GPa, the PL spectrum decreases in intensity gradually without any significant change in its line shape. When the pressure is raised up to about 20 GPa, the PL peak can hardly be resolved. Upon decompression, no NBE emission signal is retained when the pressure is released, indicating that a large number of structural defects are formed through the rearrangement of the structure with multiple transitions at room temperature.

From the above Raman results, we know that the ZnO nanosheets undergo a wurtzite to rock-salt transition at about 11.2 GPa, above which a single cubic phase is present. RS-ZnO is an indirect semiconductor with a band gap of 2.45 eV according to the results of *ab initio* calculations.[14] However, the UV emission is still observed from our ZnO nanosheets even when the applied pressure is raised up from 11 to 20 GPa. With a view to the unchanged line shapes (Fig. 3) and the regular shift of the peaks [Fig. 4(a)] of all spectra, we believe that the UV emissions above 11 GPa also come from the NBE recombination from *W*-ZnO. This is possibly due to some much smaller-size structures existed in the ZnO

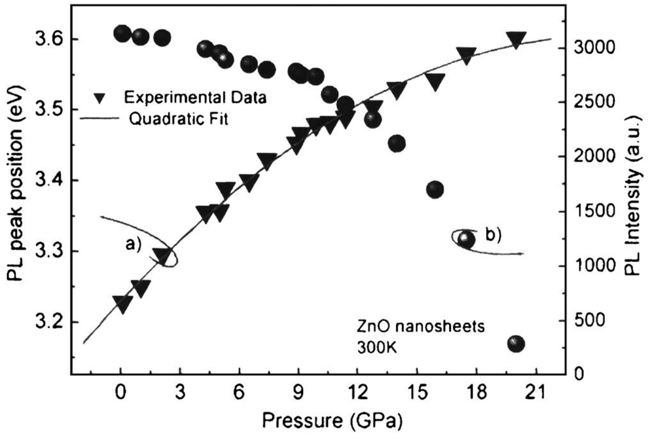

FIG. 4. (a) The variations of the energy position for the PL near-band-edge emission as a function of pressure. Experimental results are plotted by (▼). The solid line drawn through the experimental points represents the least-squares fits. (b) The intensity of the PL near-band-edge emission as a function of pressure.

nanosheets samples, which possesses a higher transition pressure than 11.2 GPa. At the same time, the smaller-size structures are too small in amount to be detected with Raman due to the much weaker signals than that of PL. The higher the pressure applied, the smaller the size of the structures could stay in wurtzite structure, which would result in a decrease in intensity of PL spectra with increasing pressure, as shown in Fig. 4(b).

The peak energies of emissions as a function of pressure were plotted in Fig. 4(a). Symbols are experimental points and the solid lines are the least-squares fits to the experimental data using the quadratic-fit function

$$E(P) = E(0) + \alpha P + \beta P^2, \tag{1}$$

where the energy E is in eV and the pressure P is in GPa. The best fits to the data yield a linear slope of 29.73 meV/GPa with a small sublinear term of -5.7×10^{-4} eV/GPa^2. The pressure coefficient of ZnO nanosheet band gap reported here is bigger than that of ZnO bulk studied by two-photon absorption,[16] where a linear pressure dependence of 25.6 meV/GPa was obtained at 6 K. We suggest that the discrepancy between our results and that reported may result from the difference of the measuring temperature, the different particle sizes of the samples, and the possible pressure-induced change of the exciton binding energy. The pressure coefficients of the NBE transitions can be approximately regarded as a signature of the direct Γ band-gap dependence on applied pressure for wurtzite ZnO, since the electronic states involved in the radiative recombination processes can be described within the framework of the effective-mass approximation and are expected to closely follow their respective band edges. Therefore, our results provide a measure of the pressure coefficient for the band gap of wurtzite ZnO.

In summary, we have investigated the transition of the *W*-ZnO to RS-ZnO for ZnO nanosheets by using pressure-dependent Raman and measured the pressure dependence of its band gap at room temperature by monitoring the NBE emission of the PL spectra. The nanosheets undergo a wurtzite to rock-salt transition with a phase-transition pressure of 11 GPa measured with Raman spectroscopy. The pressure coefficient for the direct Γ band gap of ZnO nanosheet has been deduced from the dependencies of the NBE emission on pressure. Our results yield the variation of the Γ band gap with pressure to be $\Delta E_g(P) = 29.7 \times 10^{-3} P - 5.7 \times 10^{-4} P^2$ eV. It provides a measure of the pressure coefficient for the band gap of wurtzite ZnO.

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