Photoluminescence characteristics of high quality ZnO nanowires and its enhancement by polymer covering

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We investigated the photoluminescence (PL) properties of ZnO nanowires with and without covering with polymethyl methacrylate (PMMA). Low temperature PL spectra of as-grown ZnO nanowires are dominated by near band edge (NBE) emission due to donor bound excitons and free-to-bound recombination (FB). FB emission persists till 300 K and together with free exciton emission governs the lineshape of the PL spectra. After covering with PMMA, the integral intensity of NBE emission increases about three times, indicating significantly improved excitonic emission efficiency. A model based on surface states and energy bands theory was proposed to interpret this emission enhancement. © *2010 American Institute of Physics*. [doi:10.1063/1.3291106]

ZnO is a multifunctional semiconductor material which has been exploited for short-wavelength optoelectronic applications, such as light-emitting diodes (LEDs), laser diode, photodetectors (PDs), and so on.[1–4] As is well known, the surface effects play an important role in the optical and electronic properties of ZnO related devices. Previously we have shown that the light-emitting and photodetection properties of ZnO thin films can be effectively modified by noble metal capping.[5,6] It is expected that this effect should be more pronounced in ZnO nanowires (NWs) because of their large surface-to-volume ratio. Recently, more and more attention has been concentrated on the ZnO NWs/polymer hybrid structures due to their potential applications in organic/inorganic LEDs and PDs.[7,8] In order to optimize NWs/polymer-based devices, a comparative study on the optical and electronic properties of the ZnO NWs before and after coating with polymer is of fundamental importance. Richters *et al.*[9] found a large increase in the ratio of near band edge (NBE) emission to defect-related emission of ZnO NWs at low temperatures after coating with polymers. In their letter, ZnO NWs were separated and suspended in a polymer, and the measurement was performed on the polymer thin film with embedded ZnO NWs. However, this approach was unable to compare the photoluminescence (PL) intensity because the orientation and quantity of the excited NWs have changed during the processes of separation and suspension.

Here we infiltrated polymer directly into as-grown ZnO NWs without separating the NWs from the substrate, which allows us to compare the PL efficiency purely induced by polymer capping. In this letter, we first clarify the PL mechanisms by carrying out temperature and excitation intensity dependent PL measurements, and then present detailed explanation about the effects of polymer capping on the PL characteristics.

Highly ordered ZnO NWs in our experiments were grown on *c*-plane sapphire by a vapor phase transport process.[10–12] The as-grown samples are vertically aligned NW arrays, and the ZnO NWs have very uniform diameters (220–240 nm) and length (~5 μm). After growth, the poly-

methyl methacrylate (PMMA) was covered on the surface of the ZnO NWs by spin-coating, followed by drying at 120 °C for 20 min. The PL measurements were carried out in a close-cycled He cryostat between 10 and 300 K using a He-Cd laser (325 nm line).

Figure 1(a) presents the NBE emission spectra of ZnO NWs with and without PMMA at T=10 K. The emission at 3.372 and 3.356 eV can be unambiguously assigned to the
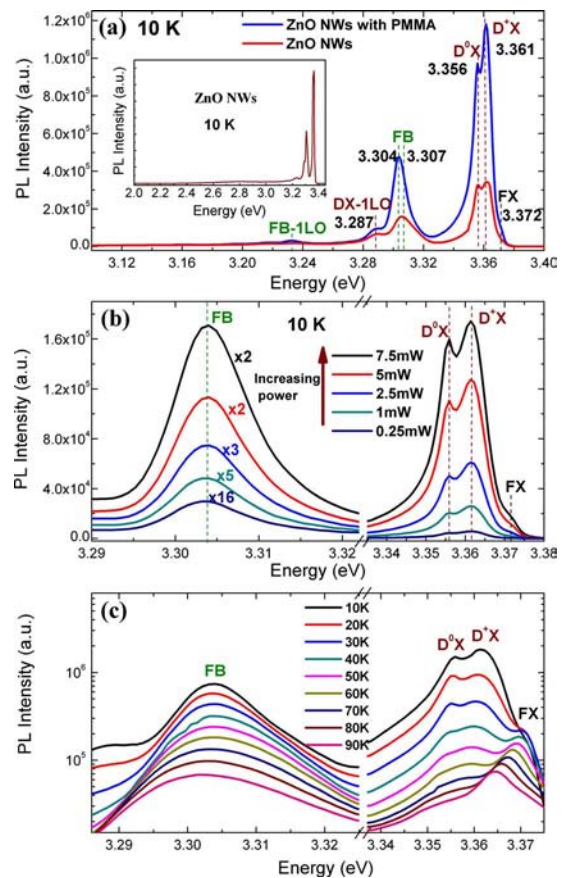

FIG. 1. (Color online) (a) PL spectra for ZnO NWs (red line) and ZnO NWs with PMMA (blue line) at T=10 K; (b) excitation intensity dependent measurement of ZnO NWs at T=10 K; and (c) the evolution of PL of ZnO NWs with temperature.

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free excitons (FX) and the excitons bound to neutral donor (D⁰X), respectively. The inset of Fig. 1(a) shows that the visible emission due to the deep level defect emission from ZnO NWs is very weak and almost unnoticeable at 10 K.

Concerning the PL band at 3.361 eV, it was primarily attributed to the D⁰X in the previous reports.[13–15] It is arguable that this emission band may be associated with Al-related donors in ZnO NWs due to the diffusion from sapphire substrate.[16,17] However, the penetration depth of ZnO for 325 nm is about several hundreds nanometers, so the excitation is just at the top of the wires while the diffusion occurs at the bottom of the wires. Considering that our NWs have length of about 5 μm, we believe that emission associated with Al-related donors due to substrate diffusion may not be the main origin. Surface donor bound exciton (SBX) emission may also occur in this spectral range, especially for nanostructured ZnO.[9,18–20] In order to clarify the origin of this peak, the excitation power and temperature dependent PL spectra measurements were carried out and the data are shown in Figs. 1(b) and 1(c). SBX band usually shows the following typical behavior:[19] it saturates at lower excitation densities than the D⁰X lines, and with increasing temperature the SBX peak intensity decreases much faster compared to the D⁰X peaks. In Fig. 1(b), the emission band at 3.361 eV does not saturate with increasing excitation power and its trend is similar with D⁰X at 3.356 eV. Meanwhile, with increasing the temperature, the intensities of both peaks at 3.356 and 3.361 eV decrease with the similar rate [see Fig. 1(c)]. This suggests that the emission band at 3.361 eV should not come from SBX, may be related to donor impurity instead. In Fig. 1(c), the intensities of both peaks at 3.356 and 3.361 eV decrease with increasing the temperature. However, the latter decreases with a rate almost the same as the former, which is unusual because normally the thermal quenching rate should be faster for emission band of excitons with smaller binding energy. This feature makes us to speculate that the emission band at 3.361 eV may come from the excitons bound to ionized donor impurities (D⁺X).[21] First, the energy position supports this assignment because usually the binding energy of D⁺X is a little smaller than that of D⁰X.[22] Second, as the temperature increases, the intensity of these two peaks decreases due to the thermal dissociation of bound excitons into free ones, as well as the ionization of donor impurities. Meanwhile, the increased number of ionized impurities may increase the probability of excitons binding to them. This can well explain the unusual thermal quenching rate of the peaks at 3.356 and 3.361 eV. Therefore, the emission at 3.361 eV should be attributed to D⁺X in our work.

In Fig. 1(a), a strong emission band on the low energy side of the D⁰X band was observed clearly at 3.304–3.307 eV. Different recombination channels have been considered as the origin of this band, such as the longitudinal optical (LO) phonon replica of FX,[13,20] donor-acceptor pair (DAP) recombination,[15,23] recombination of excitons bound to surface defect states[14,24] and free-to-bound recombination (FB).[25,26] First we argue that this line cannot be attributed to FX-1LO because the energy distance between the FX line and this emission line decreased from 65 meV (68 meV) at 10 K to 50 meV (50 meV) at 200 K for ZnO NWs (ZnO NWs with PMMA), which are smaller than the energy of an LO phonon (72 meV). This emission line may not be domi-
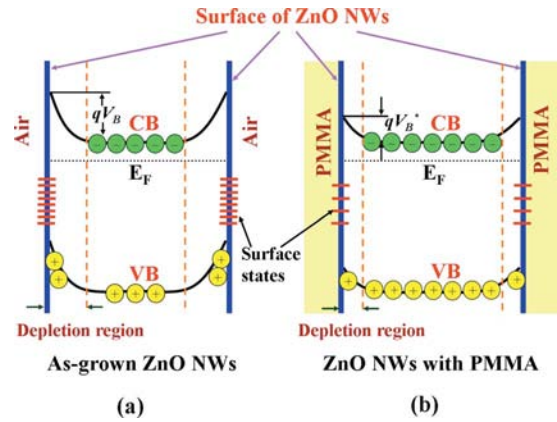

FIG. 2. (Color online) Sketch of the energy band of the ZnO NWs (a) and ZnO NWs with PMMA (b).

nated by DAP band either because the emission peak position displays almost no change with increasing the excitation power as shown in Fig. 1(b). Whereas recombination of excitons bound to surface defect states cannot be ruled out, we incline that this emission may come from FB recombination because the asymmetric lineshape on the high energy side at higher temperature as shown in Fig. 1(c). This asymmetry may be accounted for the wider distribution of free particle energies with the increase in temperature.

In order to explain the NBE emission increase by PMMA, we propose a model in Fig. 2. It has been recognized that the unintentionally doped ZnO is an *n*-type semiconductor for its intrinsic defects, such as oxygen vacancies.[27] The defects at the surface may act as adsorption sites. The adsorption of gas molecules, such as O_2 and H_2O, on the surface of NWs will trap free electrons, which results in a space charge region and band bending of the surface, as illustrated in Fig. 2(a). Consequently, photogenerated electron-hole pairs may be separated, thus the number of excitons and exciton-related emission will be reduced. The separated carriers have two channels to decay; one is nonradiative recombination, and the other one is that the excess holes at the surface tunnel into the deep level centers inside the NWs and produce deep level emission. In our sample, the deep level emission is very weak, indicating that the main decay channel for separated electron-hole pairs is nonradiative recombination. After covering with PMMA, surface modification can reduce the surface states and then decrease the built-in-barrier height (qV_B), in turn decrease the width of depletion region [see Fig. 2(b)]. So the number of separated electron-hole pairs decreases. Accordingly, the number of excitons and thus exciton related emission increase. The overall effect is equivalent to the reduction in nonradiative recombination process, which is consistent with the time-resolved PL observation conducted in noble metal covered ZnO thin films.[5] As for the origin of the redshift of FB peak position after covering by PMMA, the slight difference in binding energy of bound states and the energy fluctuation of free particles should be responsible for this trend. Meanwhile, the change of local environment (electronic properties and refractive index) may be another reason. According to the LO phonon energy of ZnO (72 meV), the peaks at 3.287 and 3.232 eV can be attributed to the 1-LO phonon replicas of DX (both D⁰X and D⁺X) and FB, respectively.
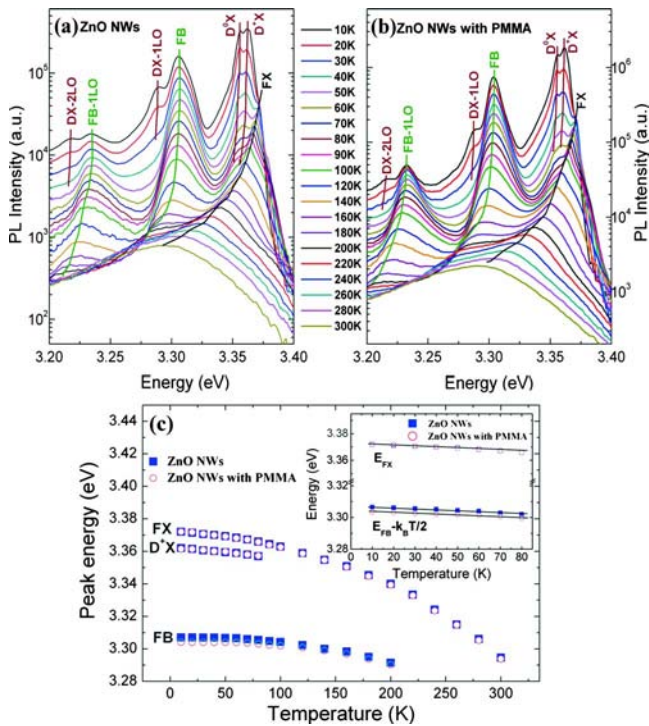
FIG. 3. (Color online) Temperature-dependent PL spectra obtained from (a) ZnO NWs and (b) ZnO NWs with PMMA; (c) the temperature-dependent peak position of the three emission bands for ZnO NWs (blue squares) and ZnO NWs with PMMA (red circles). The inset of (c) shows the temperature dependence of E_{FX} and $(E_{FB} - k_BT/2)$ from 10 to 80 K.

Figures 3(a) and 3(b) show the temperature-dependent NBE emission spectra of the ZnO NWs with and without PMMA. The main emission lines display the similar behaviors for the two samples. When the temperature increases gradually, the intensity of DX becomes weaker and the peak shifts toward lower energy. At above 120 K, the DX peaks are too weak to be identified and the FX peak becomes dominant in the spectrum. Note that the intensity of FB emission line decreases slowly with increasing temperature and it can be still seen clearly as a shoulder at room temperature. Figure 3(c) shows temperature dependence of the PL peak energies from FX, D$^+$X and FB emissions extracted from Figs. 3(a) and 3(b). In Fig. 3(c), it can be found that there is almost no discrepancy in peak energy of FX and D$^+$X before and after covering by PMMA. Meanwhile, the energy of the FB peak for the ZnO NWs with PMMA is a little smaller than that of the bare ZnO NWs by a value of 3 meV below 70 K. But at the temperature above 120 K, the peak positions of FB become identical for two samples. This phenomenon may be attributed to the fact that the effects of PMMA covering on FB emission become weaker at higher temperature due to the thermal excitation. The FB emission energy (E_{FB}) can be expressed as[23,25]

$$E_{FB} = E_g - E_B + k_BT/2, \quad (1)$$

where E_g is the band gap energy and E_B is the binding energy of the bound state. The band gap can be estimated by the PL peak of the FX (E_{FX}), and the binding energy (60 meV) of the FX. In the inset of Fig. 3(c), temperature dependence of E_{FX} and $(E_{FB} - k_BT/2)$ from 10 to 80 K were shown and $(E_{FB} - k_BT/2)$ displayed an identical temperature dependence to E_{FX}. This result is in very good agreement with Eq. (1) and confirms that ~3.307 eV emission line at 10 K PL

spectra comes from FB recombination. Furthermore, the binding energy of the bound state are also estimated about 125 and 128 meV before and after covering with PMMA. These values are comparable with that of the previous report (~124 meV).[25]

In summary, highly ordered ZnO NWs with and without PMMA have been prepared and investigated. The NBE emission of ZnO NWs at low temperatures is dominated by DX and FB emission lines. After covering with PMMA, the intensity of NBE emission increased about three times due to the decrease in nonradiative process by surface modification.

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