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Exciton recombination in ZnO nanorods grown on GaN/sapphire template

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The authors have employed variable temperature photoluminescence (PL) and time-resolved PL spectroscopy to probe the exciton recombination in high density and vertically aligned ZnO nanorods grown on *p*-type GaN/sapphire template. The low-temperature PL characterizes the dominant near-band-edge excitonic emissions from such nanorod arrays. At 4.3 K, a PL decay time of 432 ps reveals improved crystalline quality. The PL decay time shows irregular behavior due to different types of excitonic transitions dominating the PL spectra at different temperatures and a competitive effect of radiative recombination and nonradiative relaxation processes. © 2009 American Institute of Physics. [DOI: 10.1063/1.3074366]

Recently, ZnO has attracted considerable attention as a promising material for short wavelength optoelectronic devices.¹ In particular, majority of research investigations are devoted to the growth and characterization of ZnO nanostructures.^{2–6} As excitons play important roles in optical properties, the understanding of exciton recombination in ZnO nanostructures is always critical for their applications in optoelectronic device. Time-resolved photoluminescence (TR-PL) is a nondestructive technique to evaluate relaxation of optically excited states. Such measurements can also predict the radiative lifetime and charge state of defect centers associated with excitonic transitions in ZnO. The lack of reproducible *p*-type ZnO layers with high hole concentration and mobility has promoted the growth of ZnO on *p*-type GaN. Due to a small lattice mismatch between ZnO and GaN, majority of research groups is trying to realize such ZnO-based hybrid *p-n* heterojunction as an alternative pathway for optoelectronic applications.^{7–10} To obtain hybrid ZnO/GaN photonic structures, high-density, vertically aligned, and good optical quality ZnO nanorods on *p*-type GaN are desirable. In this letter, we investigate the exciton recombination in ZnO nanorods grown on *p*-GaN/sapphire templates by variable temperature PL and (TR-PL) spectroscopy.

The ZnO nanorods were grown on *p*-GaN/sapphire substrate by metal organic chemical vapor deposition (MOCVD) using a vertical cold-wall reactor. The Mg-doped *p*-type GaN used as a substrate was grown on top of 1.5 μm undoped GaN. The thickness of the *p*-GaN was about 500 nm. During the ZnO growth, the reactor pressure was kept at 1 Torr. The nanorods were grown at 450 °C for 40 min, and the precursors used for ZnO nanorods were diethylzinc (DEZn, purity 99.9995%) and pure oxygen gas (O₂, 99.9999%). The variable temperature PL measurements were carried out using a 325 nm line excitation from a He–Cd laser. The time-integrated and TR-PL measurements were conducted using the excitation of 120 fs pulses centered at 325 nm from an optical parametric amplifier, which was driven by a 1 kHz

Ti:sapphire regenerative amplifier. The total time resolution of the setup is 20 ps. The visible and ultraviolet resonant Raman experiments were performed using a JY-T64000 micro-Raman setup.

Figure 1(a) shows the cross-sectional scanning electron microscopy (SEM) image of ZnO nanorods grown on *p*-GaN

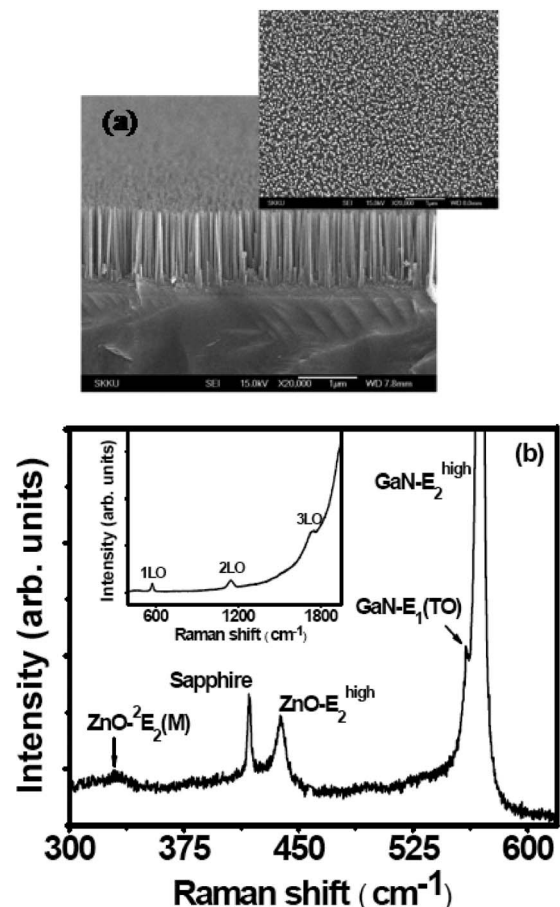


FIG. 1. (a) Cross-sectional SEM image of ZnO nanorods grown on *p*-GaN substrates. The inset shows the plane view SEM image of nanorod arrays. (b) The visible Raman spectrum observed from ZnO nanorod arrays under 514.5 nm excitation. The inset shows the ultraviolet resonant Raman spectrum recorded using the 325 nm excitation from a He–Cd laser.

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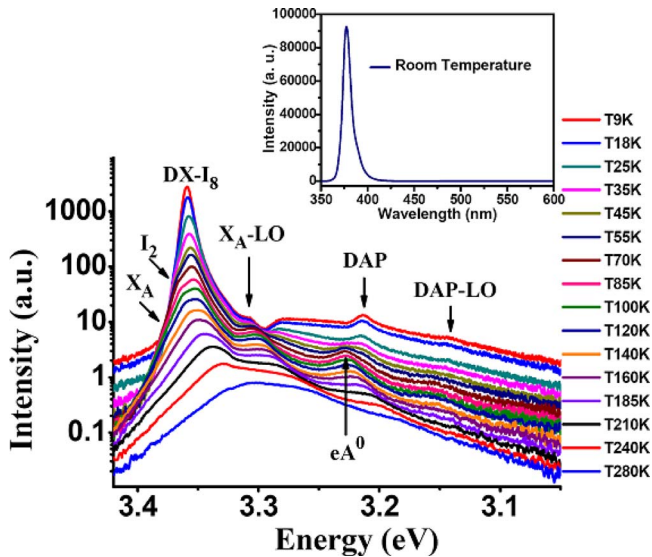


FIG. 2. (Color online) The temperature-dependent PL spectra of ZnO nanorods showing excitonic lines: X_A , I_2 , and I_8 , and the LO phonon replicas of X_A and DX emissions. The inset shows the room temperature PL spectrum from these nanorods where the deep level bands are very weak.

substrates. The inset shows the plane view SEM image. The nanorods are vertically well-aligned and are uniformly distributed. The length and average diameter of the nanorods are $1.2\ \mu\text{m}$ and in the range of 45–50 nm, respectively. The visible Raman spectrum observed from nanorod arrays shows E_2^{high} optical phonon mode at $438.5\ \text{cm}^{-1}$, suggesting that the nanorods are of hexagonal wurtzite structure [Fig. 1(b)]. The Raman peaks at 569.5 and $559.5\ \text{cm}^{-1}$ are assigned to E_2^{high} and E_1 (TO) modes from the underlying GaN template, respectively. The Raman peak from sapphire substrate is observed at $417.5\ \text{cm}^{-1}$. Additionally, the ultraviolet resonant Raman scattering measurements on these nanorods show higher-order longitudinal-optical (LO) phonon modes of ZnO up to 3rd order (1LO at $576.2\ \text{cm}^{-1}$, 2LO at $1148.5\ \text{cm}^{-1}$, and 3LO at $1737.2\ \text{cm}^{-1}$) and confirm good optical quality nanorods [inset of Fig. 1(b)]. However, for application of ZnO nanorods in optoelectronic devices, it is always vital to study their emission and exciton dynamics. In this context, we have carried out PL and TR-PL measurements at different sample temperatures.

Figure 2 shows the PL spectra of ZnO nanorod arrays grown on *p*-GaN. The room temperature PL spectrum (inset in Fig. 2) from nanorod arrays shows a strong band-edge emission at 376 nm ($3.303\ \text{eV}$). The deep level emission in the visible region (500–650 nm) is very weak. At low power laser excitation, typical ratio of band-edge PL peak intensity and intensity of deep level bands is 80:1. The strong band-edge emission with negligible deep level emission suggests high optical and crystalline quality nanorods. Furthermore, in order to probe the near-band-edge excitonic features, the PL spectra are also studied within a temperature range of 4.5–300 K. The dominant emissions from nanorod arrays at low temperature are the donor-bound exciton (D^0X) lines. At 9 K, the PL spectra are characterized by excitonic lines: X_A ($3.378\ \text{eV}$), I_2 ($3.368\ \text{eV}$: DX), I_8 ($3.358\ \text{eV}$: D^0X), and LO phonon replica of X_A .¹¹ The dominant peak I_8 ($3.358\ \text{eV}$) at 9 K observed in the PL spectrum corresponds to exciton bound to neutral donor (D^0X) and became prominent due to the incorporation of Ga impurity from the *p*-GaN template.¹² The

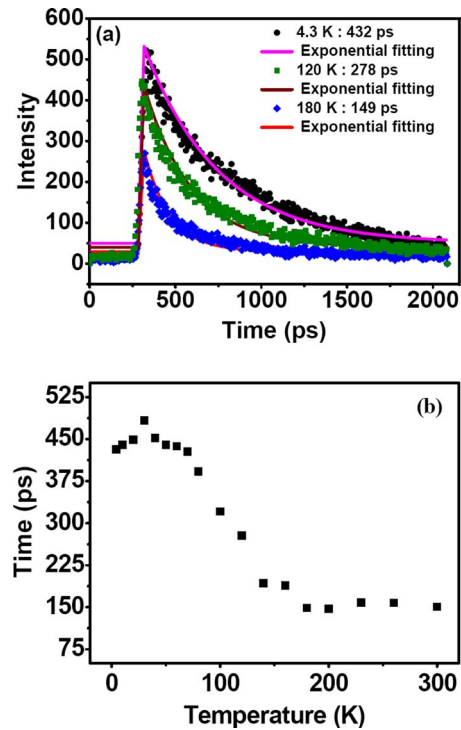


FIG. 3. (Color online) (a) The time evolution of spectrally integrated PL of ZnO nanorods measured at 4.3 K (decay of DX- I_8), 120 K (decay of DX- I_2), and 180 K (decay of FX). (b) The PL decay time as a function of temperature from 4.3 to 300 K. The PL decay times are obtained from the least square fitting of the TR-PL data at different ranges.

high energy shoulder I_2 ($3.368\ \text{eV}$) appearing in the PL spectrum is associated with excitons bound to ionized donors (DX).¹¹ The much weaker high energy shoulder appearing at $3.378\ \text{eV}$ is the free exciton (FX) emission with *A*-valence band (X_A) of ZnO. Based on the observation of strong absorption peak at $3.378\ \text{eV}$ exhibited in the transmission spectra of single crystal ZnO,¹³ the peaks at 3.378 and $3.307\ \text{eV}$ are attributed to X_A and its LO phonon replica X_A -LO having a detectable energy separation of 71 meV between them. The inhomogeneous broadening of the exciton lines is caused by point defect complexes in such low-temperature MOCVD grown ZnO nanorods. The PL peaks at 3.213 and $3.141\ \text{eV}$ having energy separation of 72 meV are assigned as donor acceptor pair (DAP) transition and LO phonon replica of DAP, respectively.^{5,11} The identification of DAP transition is further confirmed from variable temperature PL spectra, in which a new peak emerges at $3.228\ \text{eV}$ corresponding to eA^0 , and is 16 meV higher than the DAP emission.⁵ Earlier, it has been reported that the PL bands at 3.358 and $3.368\ \text{eV}$ are related to biexciton (M) and surface exciton (SX) emission, respectively.⁵ However, in our case the PL band at $3.358\ \text{eV}$ is not related to biexciton emission, as the observed decay time is very slow in comparison to fast decay time of biexciton emission,^{14,15} as shown in Fig. 3. We would also like to mention that the emission line at $3.368\ \text{eV}$ is not related to SX emission, as it shows opposite trend to SX emission, which was merged to D^0X at low temperature, and emerges prominently with increasing temperature above 40 K, revealing the emission line at $3.368\ \text{eV}$ to I_2 (DX).

Figure 3(a) shows the time evolution of spectrally integrated PL intensity of ZnO nanorods. The time-integrated PL spectrum at 4.3 K is dominated by the donor-bound exciton transitions. The decay time constant is obtained from the

least square fitting of the exponential decay curves for the temporally resolved PL spectra. The PL decay curves are usually explained on the basis of double exponential components: $I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the decay time constants of the fast and slow components, respectively. The fast and the slow components of the PL decay curves are dominated by nonradiative relaxation and radiative recombination processes of excitonic emissions, respectively. The slow component τ_2 represents excitonic radiative lifetime if the decay time constant increases with respect to sample temperature in ZnO nanostructures. In our case, we clearly observed a single exponential-type decay from the least square fitting of the TR-PL decay curves. At 4.3 K, the PL decay time of 3.358 eV DX-band obtained from these ZnO nanorod arrays is about 432 ps and is comparatively higher compared to exciton radiative lifetime reported in low-temperature grown ZnO nanorods.^{14,15} Reynolds *et al.*¹⁶ reported an exciton radiative lifetime of about 322 ps in bulk ZnO. Zhang *et al.*¹⁷ reported an exciton radiative lifetime of about 340 ps in ZnO nanorods fabricated by a vapor transport method. Recently, Wischmeier *et al.*¹⁸ reported dynamics of surface-excitonic emission in ZnO nanowires, where this PL band shows a longer decay time of 480–580 ps. The estimated value of PL decay time in our MOCVD grown samples indicates that the nanorods possess high crystalline quality. The spectral overlap of two prominent DX lines within the spectral range of 3.370–3.350 eV in these nanorods led to a decrease in the fraction of the slow/radiative decay component.

The PL decay time observed from these nanorod arrays at various temperatures is shown in Fig. 3(b). The decay time constant of DX band exhibits irregular behaviors as the temperature increases above 30 K. Within the temperature range of 4.3–30 K, the single exponential-type radiative decay of bound exciton DX- I_8 (3.358 eV) mainly represents the slow component. As seen from Fig. 3(b), the PL decay time of this DX band increases monotonously to 488 ps at 30 K, then starts to show a gradual decrease up to 392 ps at 80 K. Above 100 K, the PL decay time reduces very fast. The decay time above 180 K remains almost constant as the FX emission dominates the spectra at higher temperatures. Since the PL decay time of bound exciton became higher when temperature increased from 4.3 to 30 K, the measured decay time constant clearly represents the exciton radiative lifetime of bound exciton.¹⁹

In the temperature range of 30–80 K, the competing effects of radiative recombination and nonradiative relaxation processes led to a gradual decrease in decay time despite the observation of a single exponential decay of the bound exciton. The reduction in PL decay time at a temperature higher than 80 K can be explained on the basis of different excitonic transitions dominating the emission spectra. Although each spectrum of bound excitons decays with their respective decay time, the time-integrated PL signal shows a significant contribution from the dominant DX band within the temperature range of 4.3–80 K. Bertram *et al.*²⁰ clearly observed different lifetimes for different excitonic transitions, having maximum value for I_9 , minimum value for FX, and intermediate value for I_2 transition. In our case, as the temperature increases to 80 K, the intensity of I_2 line becomes comparable to I_8 , and thus, the value of I_2 exciton radiative lifetime at higher temperature range is difficult to estimate. At tem-

perature above 120 K, the broad FX emission at 3.354 eV dominates the integrated PL spectra, and as the lifetime of FX is very short compared to I_2 and I_8 lines, the PL decay time reduces drastically. Due to the higher surface to volume ratio, the measured decay time at high temperature is dominated by fast capture of excitons into nonradiative defect states since we have used a comparatively lower excitation density (50 μW).

In summary, we have studied the exciton recombination in high-density and vertically aligned ZnO nanorods on *p*-type GaN/sapphire template using variable temperature PL and TR-PL spectroscopy. The PL spectra revealed strong band-edge emission with negligible deep level emission, suggesting high crystalline quality nanorods. The behavior of PL decay time as a function of temperature is explained by considering different dominant excitonic transitions at different temperature ranges of PL spectra.

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