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Excitonic emissions observed in ZnO single crystal nanorods

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We report on the photoluminescent characteristics of ZnO single crystal nanorods grown by catalyst-free metalorganic vapor phase epitaxy. From photoluminescence (PL) spectra of the nanorods at 10 K, several PL peaks were observed at 3.376, 3.364, 3.360, and 3.359 eV. The PL peak at 3.376 eV is attributed to a free exciton peak while the other peaks are ascribed to neutral donor bound exciton peaks. The observation of the free exciton peak at 10 K indicates that ZnO nanorods prepared by the catalyst-free method are of high optical quality. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544437]

One-dimensional semiconductor nanowires and nanorods are potentially ideal functional components for nanometer-scale electronics and optoelectronics.^{1–3} Homogeneous and heterostructural nanowires have already been employed in various nanoscale devices.^{4,5} Among the wide variety of 1D semiconductor nanostructures,^{1–5} ZnO nanorods attract special interest for high-efficiency short-wavelength optoelectronic nanodevices, due to their large excitonic binding energy of ~ 60 meV and high mechanical and thermal stabilities. The optical characteristics of ZnO nanorods, including stimulated emissions at room temperature have recently been reported.⁶ Meanwhile, optical characterization methods such as photoluminescence (PL) spectroscopy requiring no physical contacts are useful for defect characterization of the nanomaterials since it is difficult to make reliable metal contacts on nanoscale materials. In particular, low temperature PL spectroscopy is a very sensitive tool for characterizing radiative defects.^{7,8} Nevertheless, low temperature PL spectroscopy of semiconductor nanorods has not been extensively investigated. In this letter, we report observation of both free and defect-mediated excitonic emissions from low temperature PL spectra of ZnO nanorods grown by catalyst-free, metalorganic vapor phase epitaxy (MOVPE).

ZnO nanorods were grown on $\text{Al}_2\text{O}_3(00\cdot 1)$ substrates using a low pressure MOVPE system. Details of ZnO nanorod growth are described elsewhere.⁹ For PL measurements of ZnO nanorods, a He–Cd laser (325 nm) was used as the excitation source and a grating monochromator and photomultiplier detection system were employed. Details on the PL measurements have previously been reported.¹⁰ The PL measurements in this research were performed at 10–300 K using a Displex refrigerating system.

The general morphology of ZnO nanorods was obtained using field emission scanning electron microscopy (FESEM). As shown in Figs. 1(a) and 1(b), ZnO nanorods were vertically well-aligned with uniform length, diameter, and distribution density. The diameter and aspect ratio of the nanorods are controlled in the range of 7–100 nm and 10–50, respectively.

Figure 2 shows a typical PL spectrum of high quality ZnO nanorods measured at 10 K. Several sharp peaks in the vicinity of band edges were observed at 3.359–3.376 eV, attributed to the exciton transitions. The inset in Fig. 2 shows that the near band edge emission consists of four distinct peaks at 3.359, 3.360, 3.364, and 3.376 eV with full width at half maximum (FWHM) values of 1–3 meV. Compared to the previously reported PL peak positions for thin films and bulk crystals, the PL peaks at 3.359–3.364 and 3.376 eV are tentatively attributed to neutral-donor bound exciton peaks (I_2) and a free exciton peak (X_A), respectively.^{10–13} The FWHM values of the exciton peaks for ZnO nanorods are as narrow as those for epitaxial thin films and bulk single crystals.^{11,13} On the other hand, the deep level emission, known to be related to structural defects or impurities, centered at 2.28 eV was extremely weak as indicated by an arrow in Fig. 3. The intensity ratio of the band-edge emission to the deep level emission for the nanorods is about 14 000, while the ratios for ZnO thin films were in the range of 750–1000.¹⁴ The sharp excitonic emission and very weak deep level emission peaks indicate that the ZnO nanorods are of high optical quality.

It is noted that all excitonic emission peaks at 10 K are located at the same position as previously observed in ZnO thin films.^{10–13} Thus it is believed that the PL peak shift due

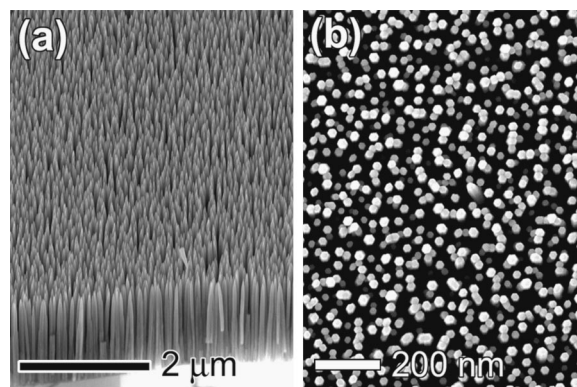


FIG. 1. (a) Vertically well-aligned ZnO nanorods with uniform length, diameter, and distribution density on the sapphire substrate. (b) The nanorods consist of hexagonal-shaped layers, which strongly suggests that the direction of nanorod growth corresponds to the c axis of the crystal structure.

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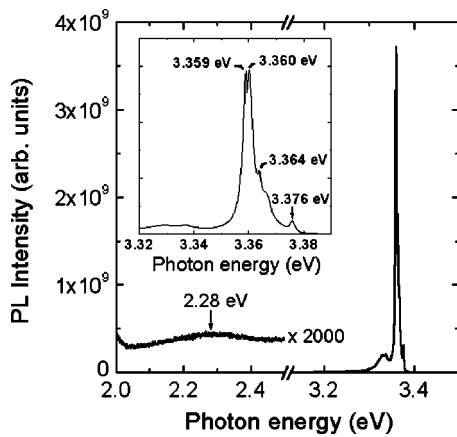


FIG. 2. PL spectrum of high quality ZnO nanorods measured at 10 K. Very weak deep level emission is observed at 2.28 eV. The inset shows that the dominant near band edge emission consists of four distinct peaks at 3.359, 3.360, 3.364, and 3.376 eV with full width at half maximum (FWHM) values of 1–3 meV.

to the quantum confinement effect does not occur in these ZnO nanorods with diameters thicker than 20 nm. The large diameters of nanorods exceeding 20 nm might provide an explanation for this.

The origins of the tentatively assigned excitonic emission peaks were further investigated by a series of PL measurements at temperatures of 10–300 K. As shown in Figs. 3(a) and 3(b), the temperature-dependent PL spectra show that the intensity of the PL peak at 3.376 eV (X_A) increased

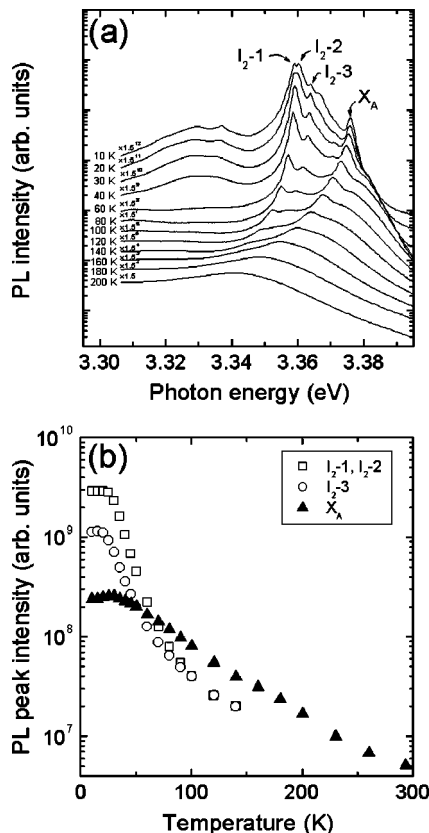


FIG. 3. (a) Temperature-dependent PL spectra of ZnO nanorods. (Data in the range of 200–300 K has been omitted for clarity.) (b) Temperature-dependent PL peak intensities of ZnO nanorods. The PL peak at 3.376 eV (X_A) corresponds to a free exciton peak and the others to bound exciton peaks.

with increasing temperature from 10 to 25 K but the intensities of the peaks at 3.364 (I_2-3), 3.360 (I_2-2), and 3.359 (I_2-1) eV decreased. This behavior presumably results from decomposition of bound excitons to free excitons due to the increased thermal energy, and hence supports the argument that the PL peak at 3.376 eV corresponds to a free exciton peak and the others to bound exciton peaks. Above 25 K, the intensities of the exciton recombination peaks also show a monotonous decrease with increasing temperature because of thermally induced dissociation of electron-hole pairs. However, in contrast to those of the two bound exciton peaks disappearing around 150 K, the free exciton peak extends to room temperature. The free exciton peak of the nanorods exhibited a FWHM of 3 meV at 10 K, almost equal to that of high quality ZnO epilayers prepared by molecular beam epitaxy.¹¹

The observation of the free exciton peak for ZnO nanorods at 10 K strongly suggests that the nanorods are of high optical quality. It has been proposed that defect-induced PL peaks are more dominant for nanorods with large aspect ratios than those of bulk materials, due to an increased number of surface states and easier incorporation of impurities. In fact, a large number of ZnO bulk single crystals and thin films have previously been reported to exhibit only a strong bound exciton peak at low temperatures below 20 K, reflecting a high concentration of defects in the materials. However, our results demonstrate that low defect concentration is still achievable even in the case of nanoscale materials despite the unfavorable circumstances.

The high optical quality of the nanorods in this research presumably results from their unique catalyst-free growth. In this case, high purity would be expected using a noncatalytic growth technique by utilizing direct adsorption of atoms on the top surface of the nanorods. The catalyst-free method excludes possible incorporation of catalytic impurities, which might occur during the condensation-precipitation process for the metal catalyst-assisted vapor-liquid-solid (VLS) method. Furthermore, nanorods are grown at 400–500 °C using the catalyst-free growth method employed in this research. This is much lower than the typical growth temperature of 900 °C required for nanowire growth by catalyst-assisted growth.¹⁵ Since defect concentration, in general, decreases exponentially with decreasing growth temperature, considerable reduction in defect concentration might have ensued.

The ability to grow high purity ZnO nanorods is expected to greatly increase the versatility and power of these building blocks for nanoscale photonic and electronic device applications. The ability to reduce defect concentrations in semiconductor nanomaterials is required for many new device applications, as already proven in thin film semiconductor electronics and photonics.¹⁶ In general, high purity single crystalline materials are prepared for many device applications because an extremely small amount of unintentionally incorporated impurities is known to significantly affect electrical and optical properties of semiconductors. Most of all, obtaining such high purity nanorods implies a significant advance toward device fabrication, because precise control of conductivity via simple impurity *in situ* doping, ion implantation, or diffusion is expected to be easy.

In summary, we investigated the optical properties of ZnO single-crystal nanorods grown by catalyst-free MOVPE. Even at the low temperature of 10 K, a free exciton peak was observed in the photoluminescence of ZnO single-crystal nanorods at 10 K and the deep level was extremely weak, indicating high nanorod optical quality.

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