Time-resolved photoluminescence of the size-controlled ZnO nanorods

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Size dependence of the time-resolved photoluminescence (TRPL) has been investigated for the ZnO nanorods fabricated by catalyst-free metalorganic chemical vapor deposition. The nanorods have a diameter of 35 nm and lengths in the range of 150 nm to 1.1 μm. The TRPL decay rate decreases monotonically as the length of the nanorods increases in the range of 150 to 600 nm. Decrease of the radiative decay rate of the exciton-polariton has been invoked to account for the results. © 2003 American Institute of Physics. [DOI: 10.1063/1.1627472]

There has been a great interest in low-dimensional light-emitting nanostructures for highly integrated photoelectronic device applications. As the size of a nanostructure approaches the exciton Bohr radius, optical properties critical to device applications, such as bandgap and photoluminescence (PL) lifetime, are affected greatly by the quantum confinement effect.[1–3]

PL lifetime is related to light–matter interaction; that is, the radiative decay of the exciton polariton and various nonradiative processes, such as leak by deep-level traps, low-lying surface states, and multiphonon scattering. There are several studies on the light–matter interaction in low-dimensional nanostructures of semiconductors.[4–8] The exciton polariton luminescence is, however, quite sensitive to the concentration of defects and structural factors of the nanostructures, and it is not easy to separate the radiative recombination and nonradiative processes.

In this letter, we report time-resolved PL (TRPL) of the size-controlled ZnO nanorods. ZnO is a wide-bandgap semiconductor enabling ultraviolet light-emitting diodes and photonic devices. It shows efficient PL at room temperature due to the large exciton binding energy of ∼60 meV.[9] ZnO can be fabricated in many different nanostructures, such as quantum dots,[10–12] nanowires,[13–18] and quantum wells,[19] and we have shown in a previous report that high quality single-crystal nanorods can be grown without using any metal catalyst.[14]

The samples were grown on $Al_2O_3(00\cdot1)$ substrates by catalyst-free metalorganic vapor phase epitaxy. Details of the ZnO nanorod fabrication has been described elsewhere.[20] A series of different size ZnO nanorods was prepared by controlling the growth time. Care has been taken to ensure the same condition other than the growth time to keep the impurity concentration constant. Samples with the growth time from 30 to 120 min were selected for the PL study. The sizes of the nanorods thus selected were determined to be 29–40 nm in diameter and 150–1100 nm in length by field-emission scanning electron microscopy, as summarized in Table I. The length of the rods increases almost linearly by the growth time with a small standard deviation. The diameter, however, stays nearly constant, with somewhat larger uncertainty.

For the optical characterization of the ZnO nanorods, time-integrated PL (TIPL) and TRPL were measured. Output of a Kerr lens mode-locked Ti:sapphire laser at 700 nm was doubled to 350 nm to serve as an excitation source in both TIPL and TRPL experiments. TRPL was measured by a time-correlated single-photon-counting system, which provides sub-10 ps time resolution with deconvolution.[20]

Figure 1(a) shows TIPL of the ZnO nanorod at room temperature. All samples reveal identical spectra with the spontaneous emission maximum at 3.26 eV. In addition, deep-level emissions are negligible in all the samples demonstrating high quality of the films, which indicates that our ZnO nanorod samples are suitable for the investigation of size-dependent PL dynamics without deep-level traps.

TRPL observed at the 3.26 eV free exciton band are shown in Fig. 1(b). It can be seen clearly that the decay rate of the PL slows down as the size increases. The TRPL can be described satisfactorily by two exponentials. The time constants and relative amplitudes from the nonlinear least-square fits are listed in Table I. The TRPL of the nanorods 600 nm and longer decays by 190 ps and 1.4 ns time constants, which are comparable to those of the TRPL of the ZnO thin film at room temperature reported previously.[20]

The TRPL spectrum reconstructed from the time profiles detected at several different wavelengths does not change over time. Slight redshifts of TRPL spectra within 100 ps

TABLE I. Sizes of the ZnO nanorods and the time constants from the two exponential fits of the TRPL. Uncertainties in the diameter and length of the ZnO nanorods are 5 and 20 nm, respectively.

Sample	Diameter (nm)	Length (nm)	τ_1 (ps)	τ_2 (ps)
1	29	159	61(44%)	291(56%)
2	40	309	52(61%)	447(39%)
3	35	479	138(42%)	786(58%)
4	36	582	190(37%)	1395(63%)
5	40	1100	167(51%)	1328(49%)

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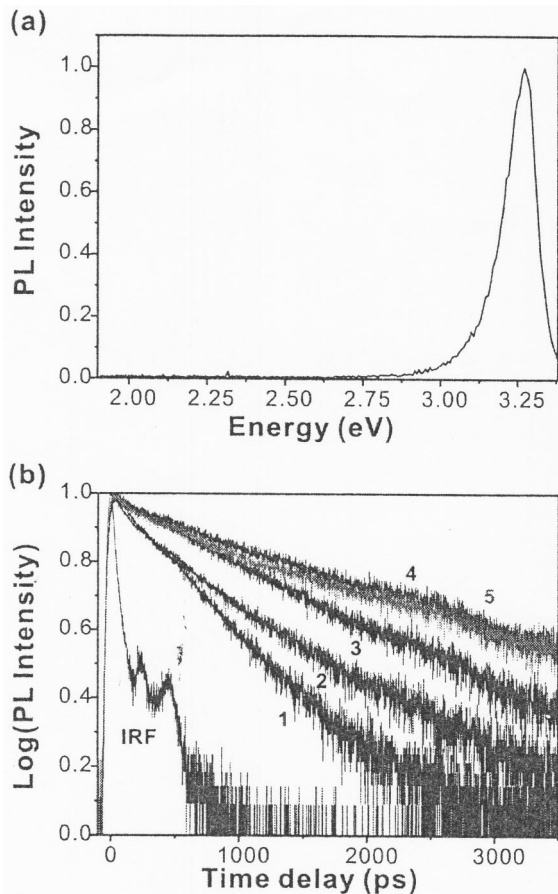
FIG. 1. Room-temperature PL spectra (a) and the TRPL measured at 3.26 eV (b) of the ZnO nanorods grown on $Al_2O_3(00\cdot1)$. The numbers in (b) correspond to the sample numbers in Table I. Instrumental response function of the TRPL apparatus is also shown.

FIG. 2. PL decay rate vs the length of the nanorods. Crosses indicate experimental values (τ_2^{-1}), and the solid line is the linear fit for the first four points.

have been observed in some of the porous silicon and CdSe quantum crystals,[4,21] which imply trapping by low-lying surface states. Surface-state trapping is not evident in this study, because the surface to volume ratio of the ZnO nanorods is much higher than those of the porous silicon and CdSe quantum crystals studied previously.

The longer time constants in the two-exponential fits can be attributed to the radiative lifetime of the exciton following the previous TRPL study of the ZnO film prepared by the same technique,[20] although the origin of the short-time constant is not certain. Correlation between the PL decay rate determined from the longer time constant and the length of the nanorod is shown in Fig. 2. Since the diameter of the rods stays nearly constant over the growth time, the abscissa may also be interpreted as the surface area or the volume of the rods. The figure reveals that the decay rate is negatively proportional to the length of the ZnO nanorod and becomes saturated at around 600 nm.

In general, a PL decay rate is a sum of the radiative and nonradiative decay rates: $\tau_{PL}^{-1} = \tau_R^{-1} + \tau_{NR}^{-1}$, where τ_{PL}, τ_R, and τ_{NR} are the PL, radiative, and nonradiative decay time constants, respectively. Therefore, the origin of the decrease in PL decay rate versus size may be radiative or nonradiative. Two possibilities may be invoked for the nonradiative processes in origin: (1) defect concentration changes over the sample in such a way that the concentration increases linearly over the growth time and (2) surface states cause non-
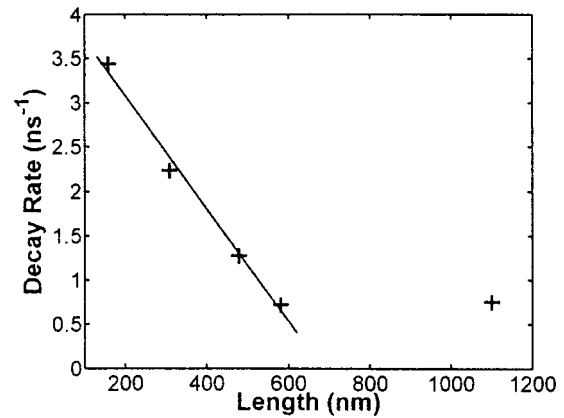
radiative decay. However, we argued against these nonradiative processes as the origin of the observed size dependence (*vide ante*). Three possibilities, radiative in origin, may be considered for the size dependence.[8] (1) Quantum confinement effect may lead to size dependent oscillator strength. The quantum confinement effect in quantum dots predicts a decreased radiative decay rate as the size increases,[22,23] as observed in this work. However, the Bohr radius of the ZnO is around 18 Å, much smaller than the diameter of the nanorods. In addition, the emission spectra are independent of the size indicating that the quantum confinement effect is negligible. (2) Scattering with the surface provides a path for an exciton to decay radiatively, which may lead to size dependence. For the ZnO nanorods employed, however, surface-to-volume ratio is nearly constant, and it may not account for the linear relationship between the decay rate and length of the rod. (3) When the size approaches the dimension of the wavelengths, exciton polariton effect becomes important, as discussed subsequently.

The light–matter interaction determined by the radiative lifetime can be distinguished into three different regions in reference to the size of nanoparticles:[8] (1) a nanoparticle smaller than the Bohr diameter of the exciton $2a_B$, (2) a nanoparticle bigger than the exciton Bohr radius but smaller than the wavelength of the light, and (3) a nanoparticle comparable to the wavelength of the light. Theoretical analyses showed that the rate of radiative recombination decreases as the size increases in regions (1) and (3), whereas it behaves oppositely in region (2).[5,6,8,22,23] According to the computational result for a quantum dot including the exciton-polariton effect, the size-dependent recombination rate is[8]

$$\Gamma_0 = \frac{\sqrt{2\pi}}{12}\,\omega_{LT}\left(\frac{2\pi}{\lambda_0}\right)^3 \langle r\rangle^3 \exp\left(-8\epsilon_b\frac{\pi^2\langle r\rangle^2}{\lambda_0^2}\right).$$

Here, ϵ_b is the dielectric constant, ω_{LT} is the longitudinal–transverse splitting frequency, and $\langle r\rangle$ is the size ($1/e$) of the exciton wavefunction. Using typical values, 1 meV for ω_{LT} and 350 nm for λ_0, a minimum radiative lifetime ~ 260 ps is obtained for a nanosphere radius of 17 nm, and it increases monotonically as the size increases.[8] The theoretical result is

in line with the present results, although the numerical values cannot be compared because of the different shape and sizes used in the model.

In conclusion, we have demonstrated by TRPL that the radiative recombination rate in ZnO nanorods depends on the size: the radiative recombination rate decreases as the length of the nanorods increases. The coupling of the excitons with the electromagnetic wave; that is, the exciton-polariton effect is invoked to account for the results. This relation between the size of nanoparticles and radiative decay time appears when the size is comparable to the wavelength of the excitation light. This may provide a design criterion for the suitable size of nanostructured electro-optic devices maintaining high efficiency.

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