

Exciton radiative lifetime in ZnO quantum dots embedded in SiO_x matrix

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Using a simple process of the deposition of ZnO thin films on SiO_x/Si substrates and subsequent thermal annealing, we fabricated ZnO quantum dots embedded in silicon oxide matrix. The ZnO quantum dots were characterized using transmission electron microscopy, and time-integrated and time-resolved photoluminescences. We measured an exciton radiative lifetime of 65 ps at 4.3 K, which is much shorter than the exciton radiative lifetime of 322 ps in bulk ZnO. The short exciton radiative lifetime can be explained in terms of exciton superradiance. © 2006 American Institute of Physics. [DOI: 10.1063/1.2207848]

ZnO has attracted much attention recently because of its potential applications in optoelectronic devices operating in the ultraviolet spectral region, owing to its direct wide band gap of 3.37 eV at room temperature.¹ Compared to other wide band gap semiconductors, ZnO has an extremely large exciton binding energy of 60 meV,^{2,3} which is much larger than the thermal energy at room temperature and therefore allows the survival of excitons at room temperature and above.⁴ Thus the excitons play an important role in the optical properties of ZnO. Excitons in geometrically confined systems exhibit different properties as compared to three-dimensional excitons as a result of the confinement.^{5–10} For example, Guo *et al.*¹⁰ experimentally found that the third order nonlinear susceptibility of ZnO nanoparticles is ~500 times larger than that of bulk ZnO. In addition to the size-dependent spectral shifts in the absorption and emission spectra, the confinement also strongly influences the exciton radiative recombination rate. Theoretically, it has been shown that the exciton-photon coupling in ZnO quantum dots (QDs) is particularly strong and the exciton radiative recombination rate drastically varies with the dot size.^{11,12} Fonoberov and Balandin^{13,14} calculated the radiative lifetime of excitons in ZnO nanocrystals and predicted the size dependence of the exciton radiative lifetime. In this letter, we report the fabrication of ZnO QDs using a simple process of the deposition of ZnO thin films on SiO_x/Si substrates and subsequent thermal annealing. We show that the geometrical confinement of ZnO QDs inside the SiO_x matrix could reduce the exciton radiative lifetime. The reduction of exciton radiative lifetime is discussed in terms of exciton superradiance.

The colloidal chemical techniques are commonly used to fabricate ZnO nanoparticles.^{10,15,16} Other methods have also been explored to fabricate ZnO nanoparticles. Kim *et al.*¹⁷ reported that the self-organized ZnO QDs could be grown on SiO₂/Si substrates using metal-organic chemical vapor deposition. Using a simple process of deposition of ZnO thin films on SiO_x/Si substrates and subsequent thermal annealing, we fabricated ZnO QDs embedded in silicon oxide ma-

trix. The sample used in the present study was prepared using the following procedure. Firstly, a SiO_x layer with thickness of 200 nm was formed on *n*-type (001) silicon wafer by thermal annealing. Then a 100 nm thick ZnO polycrystalline film was deposited onto the SiO_x layer using the filtered cathodic vacuum arc (FCVA) technique. Details of the FCVA technique, deposition procedure, and film properties have been reported elsewhere.¹⁸ Finally, the sample was annealed at 900 °C for 10 h in ambience. The sample was characterized using transmission electron microscopy (TEM), time-integrated photoluminescence (TIPL), and time-resolved photoluminescence (TRPL). TIPL and TRPL were conducted with the excitation of 150 fs pulses centered at 325 nm from an optical parametric amplifier, which was driven by a 1 kHz Ti:sapphire regenerative amplifier. The luminescence was collected in a conventional backscattering geometry. For the TIPL measurement, the PL was dispersed in a 50 cm monochromator and detected with a photomultiplier using standard lock-in amplification. For the TRPL measurement, the luminescence was dispersed in a 25 cm monochromator and detected with a streak camera. The total time resolution of the setup is 20 ps. The sample was secured in a closed-cycle He gas cryostat for temperature-variable measurements.

Figure 1 shows the TEM images of the sample. The cross-section TEM image [Fig. 1(a)] clearly shows the existence of the ZnO QDs dispersed in the amorphous SiO_x matrix. Figure 1(b) is the high resolution TEM image of a typical ZnO QD. It is seen that the QD has a crystalline structure with a dimension that measures 12.8 nm in length and 10.3 nm in height. Since the dimension of the QDs is much larger than the bulk exciton Bohr radius $a_B=1.8$ nm, this is the regime of weak confinement. Figure 1(c) is the fast Fourier transform (FFT) pattern of the ZnO QD, which is identical to the standard indexed diffraction pattern¹⁹ for the hexagonal closed packed (hcp) crystals in the [0001] beam direction [Fig. 1(d)]. From the TEM analysis, the ZnO QD has the hcp wurtzite structure with the lattice parameters $a=3.17$ Å and $c=5.17$ Å, which are in good agreement with the lattice parameter of ZnO bulk.²⁰ Using a similar method, Kim *et al.*²¹ fabricated ZnO QDs in an amorphous oxide layer. Our method is slightly different from theirs. In their method, a ZnO film was deposited directly on Si substrates

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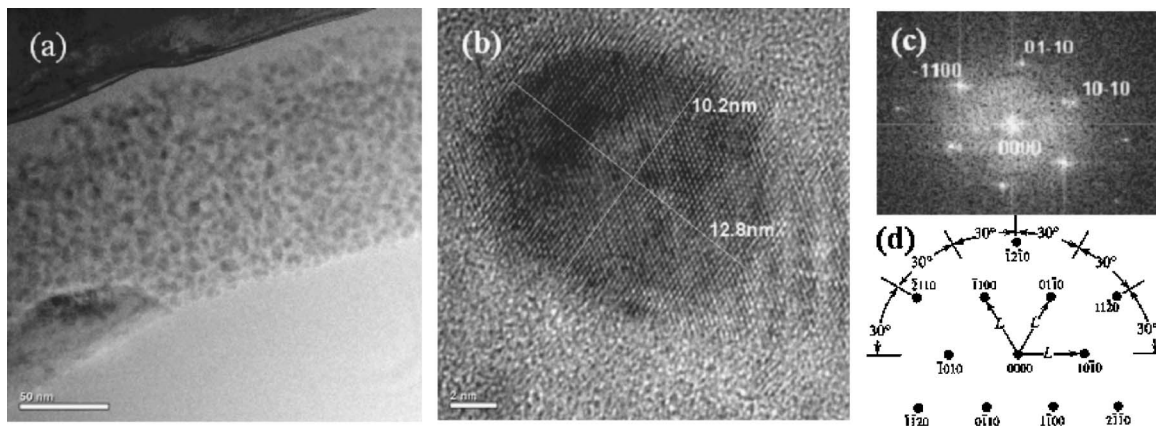


FIG. 1. TEM images of the sample. The cross-section TEM image (a) clearly shows the existence of the ZnO QDs dispersed in the amorphous SiO_x matrix. (b) The high resolution TEM image of a typical ZnO QD. (c) The fast Fourier transform pattern of the single ZnO QD. The standard indexed diffraction pattern for hcp crystals in the (0001) beam direction is also presented as a reference (d).

and then the SiO_2 layer was deposited on top of the ZnO film by plasma-enhanced chemical vapor deposition. In our method, a layer of SiO_x is grown first on Si substrate by thermal annealing and then the ZnO thin film is deposited onto the SiO_x layer.

The quantum confinement effect is most directly detected as the size-dependent spectral shift in the absorption and emission spectra. Figure 2 plots the TIPL spectrum of the ZnO QDs measured at 4.3 K. The TIPL spectrum of the as-deposited ZnO film is also plotted as a comparison. For the ZnO QDs, a PL band at 3.399 eV is observed, which blueshifts by 47 meV when compared to that of the ZnO film (3.352 eV). The blueshift of the PL peak caused by the quantum confinement can be described as follows;²²

$$\Delta E = \frac{\pi^2 \hbar^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 0.248 E_{\text{Ryd}}^* \quad (1)$$

where \hbar , R , and E_{Ryd}^* are the Planck constant, the radius of QDs, and the exciton binding energy, respectively. Taking the electron and hole effective masses as $m_e^* = 0.24m_0$ and $m_h^* = 1.8m_0$,²³ and using the bulk exciton binding energy $E_{\text{Ryd}} = 60$ meV without considering the increase in exciton binding energy due to the weak confinement, the radius of ZnO QDs is calculated to be 5.4 nm, which is in good agreement with the TEM result. It is interesting to note that the full width at half maximum (FWHM) of the ZnO QDs (38 meV) is smaller than that of ZnO film (50 meV) and the PL spectrum of ZnO QDs has a Gaussian line shape, sug-

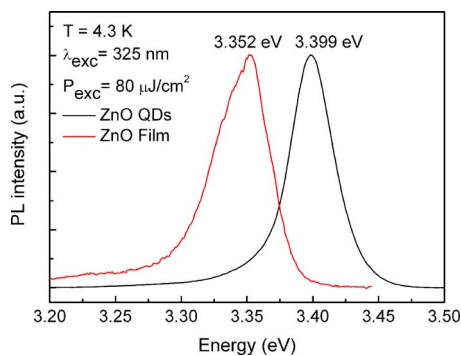


FIG. 2. (Color online) The TIPL spectrum of the ZnO QDs measured at 4.3 K. The TIPL spectrum of the as-deposited ZnO is also plotted as a comparison.

gesting the good uniformity in the size of QDs and the improvement in the crystal quality.

Figure 3(a) presents the time evolution of the spectrally integrated PL intensity of the ZnO QDs measured at 4.3 K. A lifetime of 65 ps was measured at 4.3 K, which is much shorter than the exciton radiative lifetime of 322 ps in bulk ZnO.²⁴ We now discuss whether the short decay time we measured can be explained by nonradiative recombination effects. It is well known that a short PL decay time at low exciton density with weak excitation can be caused by the dominance of nonradiative recombinations. Such a mechanism would cause a nonlinear increase in the time and spectrally integrated PL intensity with the excitation intensity.²⁵ However, our measurement, as shown in Fig. 4, reveals a linear dependence of the time and spectrally integrated PL intensity on the excitation intensity. The linear behavior of the dependence evidences that the exciton radiative recombination is the dominating channel for the carrier recombination process. To further ensure that the measured shorter lifetime was not caused by nonradiative recombinations, we

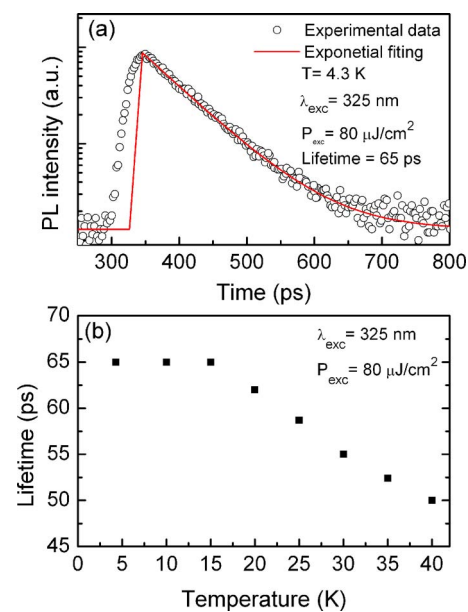


FIG. 3. (Color online) The time evolution of spectrally integrated PL of ZnO QDs measured at 4.3 K (a) and the exciton lifetime as a function of temperature (b).

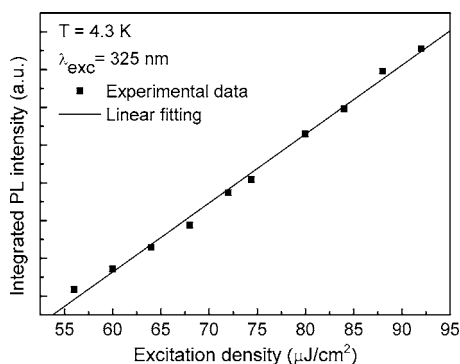


FIG. 4. The time and spectrally integrated PL intensity (solid squares) as a function of excitation density. The linear fitting (solid line) is also plotted in the figure.

measured the exciton lifetimes at different temperatures, which is shown in Fig. 3(b). If the recombination process was dominated by nonradiative channels, the lifetime would decrease with increasing temperature, since the nonradiative channels would play a more important role with increasing temperature. However, within the experimental uncertainties, the measured lifetimes do not change below 15 K. We also found that the time and spectrally integrated PL intensity remains constant below 15 K. We therefore conclude that the exciton radiative recombination dominates the recombination process below 15 K and the measured lifetimes are exciton radiative lifetimes.

We now discuss the mechanism of the short exciton radiative lifetime. As mentioned earlier, in addition to the size-dependent spectral shifts in the absorption and emission spectra (as is seen in Fig. 2), the confinement also strongly influences the exciton radiative recombination rate. Theoretically, it has been shown that the exciton-photon coupling in ZnO quantum dots (QDs) is particularly strong and the exciton radiative recombination rate drastically varies with the dot size.^{11,12} Fonoberov and Balandin^{13,14} calculated the radiative lifetime of excitons in ZnO nanocrystals and predicted the size dependence of the exciton radiative lifetime. For the dots of 5 nm, they predicted an exciton radiative lifetime of 38 ps. The exciton radiative lifetime of 65 ps we measured at 4.3 K is in reasonable agreement with their prediction. Actually, the short exciton radiative lifetime can be explained in terms of exciton superradiance. Superradiance originates from the fact that for systems small compared to an optical wavelength where all oscillator strength is cooperated in one collective superradiant excited state. This leads to an enhancement of the optical transition oscillator strength and thus to a shortening of the excitation radiative lifetime. Exciton superradiance has been studied in semiconductor

nanocrystals^{8,9} and other geometrically confined systems. Kayanuma²² theoretically studied the quantum-size effects of Wannier excitons in semiconductor nanocrystals and found that the exciton radiative lifetime in the weak confinement region (this is just the present case) decreases rapidly with the size of the nanocrystal as a result of exciton coherence effect, in other words, the exciton superradiance.

In summary, using a simple process of the deposition of ZnO thin films on SiO_x/Si substrates and subsequent thermal annealing, we have fabricated ZnO QDs embedded in silicon oxide matrix. The ZnO QDs have been characterized using TEM, TIPL, and TRPL. We measured a short exciton radiative decay time of 65 ps at 4.3 K. Our result can be explained in terms of exciton superradiance.

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