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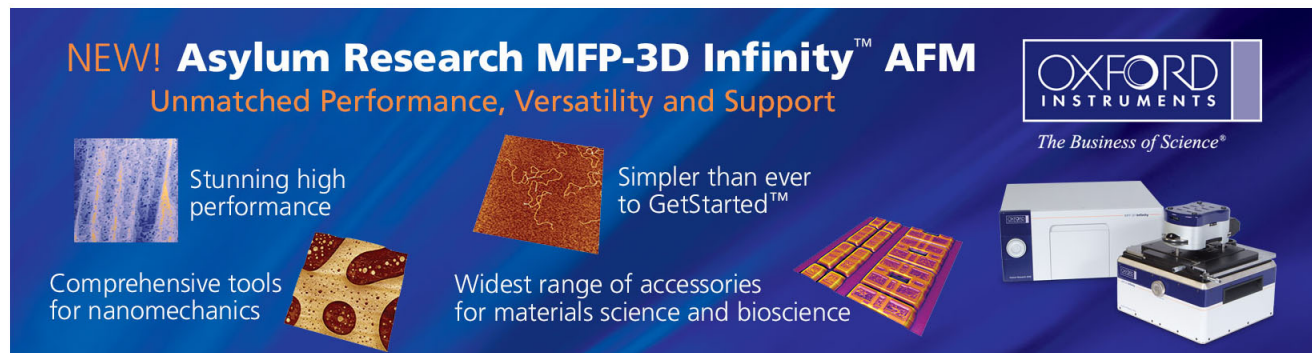
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Properties of photoluminescence in type-II ZnTe/ZnSe quantum dots

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Temperature and time evolution of the photoluminescence (PL) intensity of bimodal ZnTe/ZnSe type-II quantum dots (QDs) were investigated. A particular temperature dependence of PL was observed in large QDs. PL decay of small QDs is composed of a faster initial component and a slower tail component whereas PL decay of large QDs simply comprises a fast component. All phenomena could be understood consistently by considering charge carrier transfer mechanism, band-bending effect, and the existence of nonradiative centers in the bimodal type-II QD array. We show that excitons play an important role in the emission properties of a self-assembled type-II QD system. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189029]

Quantum dots (QDs) have attracted much attention because of their potential applications in optical and optoelectronic devices.¹⁻³ However, it has been reported that the photoluminescence (PL) of a QD ensemble quenches when the temperature is increased above a given temperature.^{4,5} This leads to a reduction of the spontaneous emission yield at room temperature for QD-based emitters. By far, research on self-organized QDs was mostly done in a type-I system grown under the Stranski-Krastanov mode.⁴⁻⁷ Few reports of type-II II-VI QDs grown under the Volmer-Weber (VW) mode could be found.^{8,9} Recently, type-II ZnTe QDs in a ZnSe matrix have been grown under the VW mode by molecular beam epitaxy (MBE).⁹ In this letter, we present a study of the PL quenching of the bimodal type-II ZnTe QD array grown by MBE. Temperature-dependent PL intensity exhibits a particular thermally activated redistribution of charge carriers within the bimodal type-II QD array. It was found that QDs with different size distributions exhibit different PL decay processes. All phenomena could be explained by considering the charge-carrier transfer mechanism, band-bending effect, and the imperfections in the type-II QD crystal.

Self-assembled ZnTe QDs were grown on a ZnSe buffer layer by a Veeco-Applied-EPI 620 MBE system at 300 °C. The average coverage of ZnTe for the sample studied here is 2.6 monolayers (MLs).⁹ The 325 nm line of a He-Cd laser was used to generate the PL spectra. Photoluminescence excitation (PLE) spectra were taken with a monochromatic light from a xenon lamp. The time-resolved PL spectra were measured using a GaN diode laser (408 nm) with the pulse duration of 50 ps as the excitation source. The collected luminescence was dispersed by a grating spectrometer and detected with a high-speed photomultiplier tube, followed by a personal computer (PC) plug-in time-correlated counting card. The PL signal is dispersed using a monochromator and a photomultiplier tube is used to collect the emitted light.

Figure 1(a) shows three emission peaks at 2.80, 2.38, and 1.98 eV in the 10 K PL spectrum from the sample. PL emission at 2.80 eV is attributed to the near-band-edge emission from the ZnSe buffer layer. To understand PL results further, PLE measurements were performed. The PLE spectra with detection energies set at 2.38 and 1.98 eV are shown in Figs. 1(b) and 1(c), respectively. In both spectra, beside the steep increase of PLE intensity at around 2.8 eV due to the onset of the ZnSe fundamental absorption, additional peak structures were also detected. There is no absorption corresponding to the ZnTe epilayer (2.4 eV at 10 K) in the PLE results. Thus, this implies the absence of wetting layers in the sample. The corresponding peak at 2.59 eV in Fig. 1(b) shows a large Stokes shift of 210 meV with respect to PL peak energy at 2.38 eV. Similarly, the Stokes shift between the PLE peak at 2.18 eV and the PL peak at 1.98 eV is as large as 200 meV. By carefully comparing the PL spectrum with the PLE spectra, the broad structure near 2.38 eV

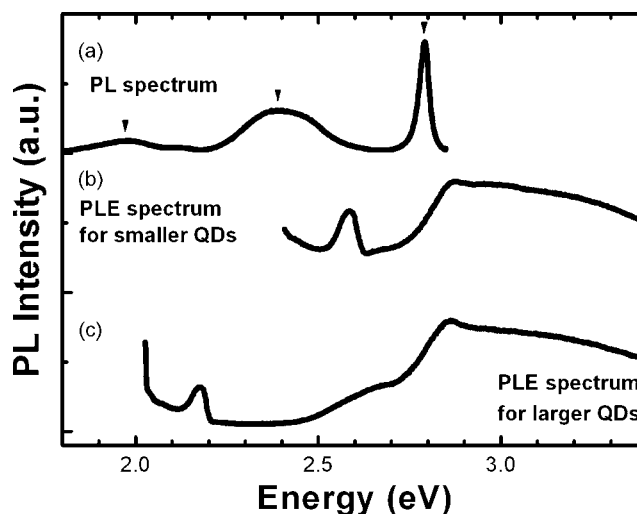


FIG. 1. Normalized PL spectrum (a) and PLE spectra (b), (c) of the ZnTe/ZnSe QD sample at $T=10$ K. The detection energies for (b) and (c) are 2.38 and 1.98 eV, respectively.

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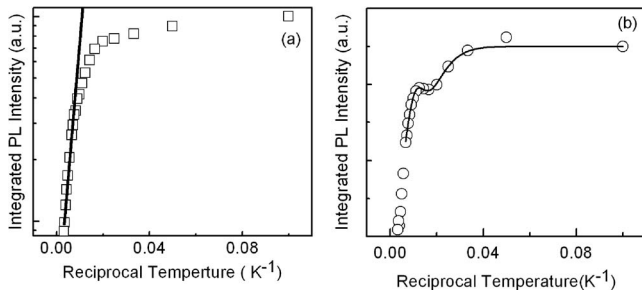


FIG. 2. Experimental (open circles) and calculated (solid line) temperature dependence of the integrated PL intensity of small QDs (a) and large QDs (b).

is a signature of PL from small ZnTe QDs, while the additional peak near 1.97 eV on the lower energy side of the PL spectrum is believed to be from the large ZnTe QDs. In Fig. 1, it should be emphasized that the PLE peak energy decreases across the energy gap of ZnTe of 2.4 eV with the increasing dot size, which is unusual for type-I heterostructures. This behavior is explained by the type-II band alignment in which the transition between the ground level of the bulk ZnSe (conduction band) and the top of the valence band of the ZnTe QD is taken into account.¹⁰ This result is a direct confirmation of the type-II band alignment of the present ZnTe/ZnSe heterostructure grown under the VW mode based on the PLE and PL measurements.¹¹

Figures 2(a) and 2(b) show the temperature dependence of the integrated PL intensity of small QDs and large QDs, respectively. The PL from the small ZnTe QDs becomes dominant (not shown) at room temperature, while the PL from the large ZnTe QDs becomes invisible or convolutes with that from the small ZnTe QDs. Figure 2(a) shows a typical behavior for thermally activated nonradiative recombinations of the small QDs. The activation energy for thermally activated nonradiative recombinations can be obtained by the relation, $I_{\text{PL}} = I_0 \exp(E_a/kT)$. Here T is the temperature, k is the Boltzmann constant, I_0 are constants, and E_a is the activation energy.¹² The activation energy obtained by this method is usually considered as the total binding energy,¹³ which includes the confinement energy and the exciton binding energy. The total binding energy, which is given roughly by the difference between the energy gap of the ZnSe (2.8 eV) and the PL energy from the QDs (2.38 eV) is around 0.42 eV. However, in our experiment, we found that the activation energy was 33 meV. This energy is an order of magnitude smaller than the above estimated total binding energy. Similar results have been found in the ZnTe/ZnS QDs,¹⁴ where the exciton binding energy was attributed to determine the quenching of the PL in the ZnTe/ZnS system instead of the total binding energy. For the case of ZnTe/ZnSe here, there is little (or no) confinement of the electron in ZnTe due to the type-II band alignment of the system. Thus, the energy required to quench PL is the energy required to break up the exciton. Therefore, this feature reveals that the exciton binding energy determines the quenching of the PL in the type-II ZnTe/ZnSe heterostructures.

From Fig. 2(b), the integrated PL intensity of the large QDs with increasing temperature first decreases above 30 K, then increases between 50 and 80 K, and finally decreases again for T higher than 80 K. It is noticed that the PL quenching of small QDs and the PL increasing of large QDs start simultaneously, when the temperature exceeds 50 K.

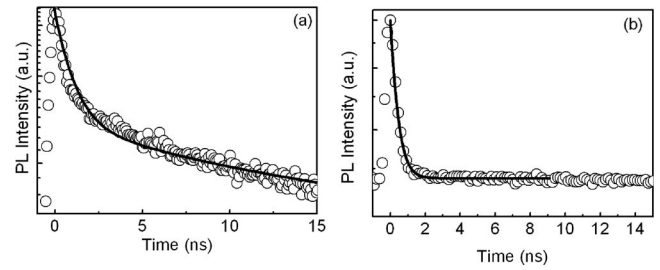


FIG. 3. Experimental PL decay (open circles) of small QDs (a) and large QDs (b) taken at the PL peak energy. The solid lines are calculated results.

Thus, the charge carriers, thermally excited out of the small QDs could be retrapped in the large QDs. As the temperature increases (above about 50 K), the charge carriers captured in the ground state of the small QDs are able to be thermally excited out of the QDs. Part of the escaped charge carriers is then recaptured in the large QDs, leading to an increase of the PL intensity of the large QDs between 50 and 80 K. The PL intensity of the large QDs decreases above 80 K because of the onset of the nonradiative recombinations. The previous work by Saint-Girons and Sagnes¹⁵ reported similar behaviors of the PL intensity of two QD populations found in the bimodal InGaAs/GaAs QD array. Accordingly, the activation energy associated with these nonradiative recombinations could be deduced from the fit of the experimental data of Fig. 2(b) with the rate equation for the PL intensity $I_1(T)$ of the large QDs at a given temperature T :¹⁵

$$I_1(T) = I_1(0) \frac{1}{[1 + C_1 \exp(-E_{a1}/kT)]^2} \times \left(1 + C \frac{C_2 \exp(-E_{a2}/kT)}{1 + C_2 \exp(-E_{a2}/kT)} \right), \quad (1)$$

where k is the Boltzmann constant, $I_1(0)$ is the PL intensity of the large QDs at $T=0$ K, C is the ratio of the charge carriers in the large QDs to that in the small QDs, C_1 is ratio of the nonradiative recombination rate in the large QDs to the radiative recombination rate in the small QDs, C_2 is the ratio between the thermal escape rate of charge carriers out of the small QDs to the barrier and the radiative recombination rate in the small QDs, E_{a1} is the activation energy of the nonradiative recombination centers in large QDs, and E_{a2} is the activation energy for the carrier escaping out of the small QDs. The solid line in Fig. 2(b) shows the best fit to the experimental data with Eq. (1). The activation energy for the nonradiative recombination centers in large QDs was found to be 16 meV. It corresponds to the exciton ionization and the possible successive nonradiative recombinations with the centers located in the interfaces, the immediate vicinity between QDs, and the barrier. Thus, the particular temperature dependence of the integrated PL intensity of the large QDs is understood.

The experimental PL decay profiles (open circle) measured at main peaks for the small and the large dots are shown in Figs. 3(a) and 3(b), respectively. From Fig. 3(a), the overall signals of the small QDs were seen to be better fitted by the thermalized stretching exponential line shape¹⁶ $I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)^\beta$, where $I(t)$ is the PL intensity at time t , I_1 and I_2 are $I_1(0)$ and $I_2(0)$, respectively, β is the scaling parameter that is related to the dimensionality of the localizing centers, τ_1 and τ_2 are the initial lifetimes.

The fitting results are shown in Fig. 3(a) with time constants τ_1 and τ_2 of 0.9 and 21 ns, respectively. The stretching parameter $\beta=0.6$ means that the localized states have spatial extension broader than the Lorentzian form in the energy space.¹⁷ These results support the staggered lineup model of the ZnTe/ZnSe QDs inferred by the PLE measurements. After the excitation, electrons and holes are generated in the ZnSe region followed by a process of hole capturing into the ZnTe dot. A dipole layer is formed between the holes in the ZnTe dots and the electrons attracted from the surrounding ZnSe regions. This field-induced band bending will confine the electron wave function closer to the ZnTe dots. Thus, the faster time constant is attributed to the increased spatial overlap due to the band-bending-induced electron confinement. When the majority of the carriers have recombined, the band-bending effect¹⁸ is negligible and the electron wave function is more spread out into the ZnSe regions. This will lead to a slow radiative recombination process between the holes in ZnTe dots and the electrons in ZnSe regions. The following stretched exponential decay probably shows a manifestation of the type-II excitonic recombination process. While the large QDs [Fig. 3(b)] only show a fast exponential decay with a decay time constant of 0.4 ns, the absence of the slow radiative component in the PL decay of the large dots could be understood if the nonradiative centers located in the immediate vicinity of the large QDs are considered. Some studies report on the presence of this kind of defect,¹⁹ which could be associated with the QD formation.²⁰ If only the quantum confinement effect is considered, the reduced spatial overlap is expected in the large QDs due to the reduced penetration of the hole wave function into the adjacent layers. And this can result in that the large QDs will show a slower decay than that of the small QDs in the recombination processes. In the present case of the large QDs, the strain-induced nonradiative recombination centers are likely to make the physics different. The nonradiative recombination centers first come into play with the carrier trapping, leading to a shorter decay time for the initial radiative recombination. After the faster initial radiative recombination, the process of slow radiative recombination will compete with the nonradiative recombination via the defect centers. Thus, from the results of the time-resolved PL measurements, we attribute the activation energy, 16 meV, obtained by Eq. (1) to the nonradiative recombination activation energy.

In conclusion, temperature dependence and time evolution of the PL intensity of a bimodal ZnSe/ZnTe QD array were studied. It was found that the large QDs show a particular temperature dependence to the PL in which the PL intensity first decreases slowly, then increases and finally decreases rapidly. This result could be understood by the mechanism that the charge carriers, thermally ionized and diffusing out of the small QDs could be retrapped in the QDs

with larger size populations. In addition, we have shown that from the study of the quenching of the PL, the breaking up of the exciton is responsible for the quenching of the PL at high temperatures. All phenomena could be understood by considering the charge carrier transfer mechanism, band-bending effect and the nonradiative recombination centers in the bimodal type-II QD array. Our results shown here are expected to be important for the understanding of the optical properties in type-II semiconductor nanostructures.

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