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Time resolved photoluminescence studies of Zn–Se–Te nanostructures with sub-monolayer quantities of Te grown by molecular beam epitaxy

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We investigate triple-delta-doped ZnSe:Te samples grown with different Te/Zn flux ratios using time-resolved photoluminescence (TRPL). We show that the properties of the TRPL of both samples are consistent with the presence of quantum islands with a type-II band alignmrnt. Moreover, from the comparison of the PL, we show that higher Te/Zn flux ratio during the growth leads to the formation of larger quantum islands.

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1 Introduction Zn–Se–Te systems have been of great interest both for their applications in light emitting devices and for interesting optical properties related to isoelectronic bound excitons (IBE). Recently it has been shown [1] that, in a so-called triple-delta-doped ZnSe:Te system (denoted further as δ^3-ZnSe:Te, for growth details see Ref. [2]), there is formation of type-II quantum islands (QI), which contribute to photoluminescence (PL) with the maximum at ~2.46–2.51 eV ("green band"). In this paper, we investigate the effect of Te/Zn flux ratio used during the growth on such quantum structures using time-resolved photoluminescence (TRPL). Specifically, we compare two samples grown by molecular beam epitaxy: sample A grown with a Te/Zn flux ratio of ~0.44 and sample B grown with a Te/Zn flux ratio of ~0.26. Both samples were grown with the same Te flux. We shall discuss the spectrally resolved time-dependent PL and the PL decay characteristics as well as their dependence on excitation intensity and temperature (T). We shall show that the PL of these two samples originates from type-II quantum islands (QIs) and that the higher Te/Zn flux ratio and/or lower Zn fluxes leads to larger QIs.

2 Spectrally-resolved pulsed laser photoluminescence In Figs. 1(a) and (b), we show the spectrally-resolved pulsed laser PL taken at different time delays with respect to the laser pulse for samples A and B, respectively. For sample A, the PL spectra (Fig. 1(a)) at shorter delay times are dominated by a broad peak at ~2.6 eV, which continuously shifts to the red with the increasing delay time. We attribute this band to excitons in type-II QIs [1]. The PL shift with the delay time has been observed in type-II quantum dots and attributed to time-dependent band bending effect (see, e.g. Ref. [3]). We note that the observed peak position at the highest excitation intensity is substantially higher than the peak energy usually observed for the "green band" in ZnSeTe alloy, but still below the PL associated with IBE due to Te_2 pairs. We believe that it is due to the strong band bending under high excitation conditions of a pulsed laser; such an effect leads to the formation of higher energy levels for carriers (electrons in this case) and

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thus to the blue-shift of the PL [4] compared with that observed in cw PL experiments. We note that the cw PL of these type-II QIs shifts as a function of the excitation intensity [1] too, as expected for such systems [4]. For sample B, this type-II QI-related PL has a very weak intensity and appears only at the delay times larger than 10ns as a low-energy shoulder on the peak due to excitons bound to Te_2 isoelectronic centers [2]. Therefore, the shift of this type-II QI-related PL in sample B is more difficult to observe. Nonetheless, considering that sample A has stronger type-II QI-related PL than sample B and that the shift of the PL energy also depends on the size of the type-II nanostructures [4], we suggest the existence of larger type-II QIs in sample A.

3 Time decay of photoluminescence To confirm our suggestions we studied the time decay characteristics of the PL. The results are shown in Figs. 2(a) and (b) for sample A and B, respectively. Under high excitation intensities, the observed PL exhibits a non-exponential decay but approaches a single exponential as time elapses. As the excitation intensity decreases, the decay of the PL also approaches a single exponential, which is parallel to the one observed under the high excitation conditions at the longer times.

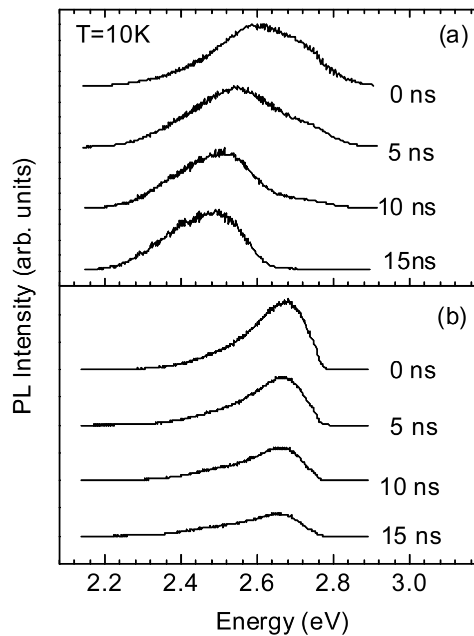

Fig. 1 Spectrally-resolved pulsed laser PL of (a) sample A and (b) sample B with various delay times at $T = 10$ K.

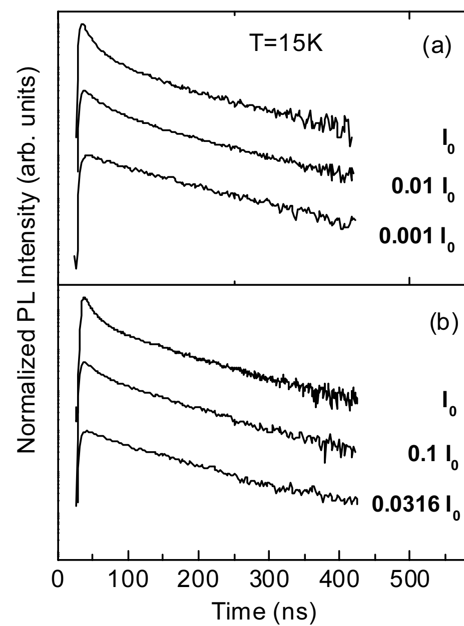

Fig. 2 The PL decay of (a) sample A and (b) sample B under various excitation intensities at $T = 15$ K

Such behavior is easily understood within the model of type-II QIs. Indeed, in type-II nanostructures the photo-generated carriers create electrical field that leads to the band bending, the magnitude of which depends on the carrier concentration [4]. At very high carrier concentrations (strong excitation) the band bending results in strong overlap of electron and hole wave-functions and thus in a faster decay. As time passes, the carrier concentrations decrease, the wave-function overlap becomes weaker and the decay becomes slower [5]. After the recombination of most of the photo-generated carriers the band-bending effects become negligible ("flat bands"), leading to a single well-defined decay time. The PL decay under the "flat bands" condition should also be observed under weak excitations, when the concentration of photo-generated carriers is low. Indeed, this is the case (Fig. 2).

Furthermore, from Fig. 3 it can be clearly seen that the spectrally-resolved pulsed laser PL of sample A, which is taken under high excitation intensity but at longer delay time, is identical to that obtained

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under weaker excitation but without a delay, confirming our conclusions above. Therefore, in further discussions we take the decay time obtained at lower excitation intensities as the characteristic lifetime (τ) of electron-hole pairs in our system.

We have estimated that τ_A (the characteristic lifetime for excitons in sample A) and τ_B (the characteristic lifetime for excitons in sample B) have values of ~95 ns and ~ 86 ns at $T = 15$ K, respectively. The fact that $\tau_A > \tau_B$ is due to the existence of larger QIs in sample A, where the overlap between the electron and hole wavefunctions is weaker due to the larger spatial separation, resulting in the smaller oscillator strength.

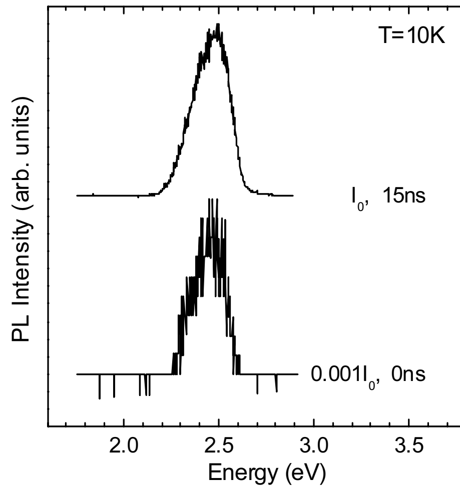

Fig. 3 Comparison of the spectrally-resolved pulsed laser PL of sample A with maximum excitation intensity (I_0) and longer delay time with lower excitation intensity and shorter delay time.

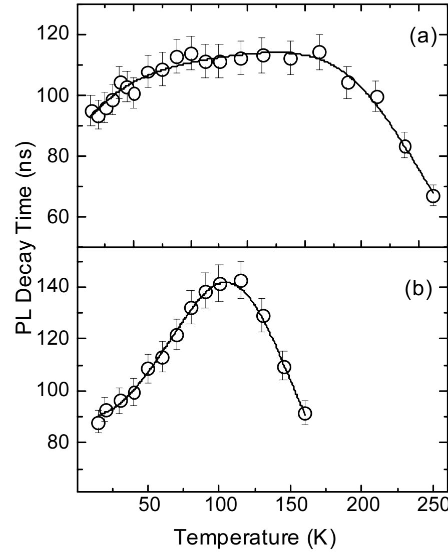

Fig. 4 PL decay time of (a) sample A and (b) sample B as a function of temperature. The circlces represent the experimental data and the solid lines are the fitting results using the formula (see text)

We next discuss the temperature behavior of PL decay. Plotted in Figs. 4(a) and (b) are the decay times as functions of temperature for sample A and B, respectively. As seen from the figures, both τ_A and τ_B increase with the increasing temperature up to 170 K and 115 K, respectively. Such increases can be explained as follows. As the temperature rises, the weakly bound electrons are ionized, and as a result, are away from the strongly localized holes for an increasing fraction of their lifetimes, which in turn will lengthen the PL decay time. We note that such an explanation is valid provided that the non-radiative processes are negligible. Indeed, from cw PL studies [1], the PL intensity is relatively constant during the temperature intervals of interest.

The increase of τ with temperature was also observed for certain systems with isoelectronic centers (see, e.g. ZnTe:O [6]) due to the similar effect, and it was fitted with the formula [6]

$$\tau_r = \tau_r^*/[1 - C\exp(-\varepsilon_{e\text{-}h}/kT)] \tag{1}$$

where τ_r^* is the radiative decay time at $T = 0$ K, C is a constant, $\varepsilon_{e\text{-}h}$ is the characteristic energy that is of the order of the electron-hole binding energy, and k is the Boltzmann constant. Taking into account the contribution from the non-radiative process, we fit the experimental data (τ) with the following formula

$$\tau = \{\tau_r^{-1} + [\tau_{nr}^*\exp(\varepsilon_{nr}/kT)]^{-1}\}^{-1} \tag{2}$$

where τ_{nr}^* is the characteristic non-radiative decay time and ε_{nr} is the activation energy of the non-radiative process. The solid lines in Figs. 4(a) and (b) are the fitting results obtained using Eq. (2), with

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$\varepsilon_{e\text{-}h}^{(A)} \approx 2$ meV for sample A and $\varepsilon_{e\text{-}h}^{(B)} \approx 8$ meV for sample B. In the type-II nanostructures, $\varepsilon_{e\text{-}h}$ is lower than the free exciton binding energy due to the existence of energy barriers separating the electrons and holes [7]. Indeed, the values of $\varepsilon_{e\text{-}h}$ obtained for samples A and B are significantly lower than the free exciton binding energy in either ZnSe (~20 meV [8]) or ZnTe (~13 meV [8]). Furthermore, one would expect lower exciton binding energies for larger type-II QIs due to the weaker overlap of electron and hole wavefunctions. Indeed, $\varepsilon_{e\text{-}h}^{(A)}$ is less than $\varepsilon_{e\text{-}h}^{(B)}$, which confirms our conclusion that sample A has larger type-II QIs.

Additionally, we would like to compare our results with those obtained by Akimova *et al.* [9] who reported $\tau \approx 35$ ns at 77 K for the green band in the $ZnSe_{0.98}Te_{0.02}$ alloy. This value is significantly lower than 114 ns and 132 ns obtained for samples A and B at 80 K (Fig. 4), respectively. Such an enhancement in the PL lifetime is due to the spatial separation of electrons and holes in type-II nanostructures.

Finally, we would like to note that although the contributions from Te isoelectronic centers cannot be excluded, the type-II QIs play an dominant role in the optical properties as shown above.

4 Summary In summary, we have investigated δ^3-ZnSe:Te samples grown with different Te/Zn flux ratios using time-resolved photoluminescence. We have shown that the PL behavior of both samples is consistent with the type-II nanostructures (quantum islands). Moreover, from the comparison of the PL, we have shown that the sample grown with higher Te/Zn flux ratio has larger quantum islands. Additionally, from the temperature-dependent studies, we have obtained the electron-hole binding energy of ~2–8 meV for our samples.

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