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Quantum structures in Zn–Se–Te system containing submonolayer quantities of Te

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In this paper we show that a multilayer Zn-Se-Te system, grown by molecular beam epitaxy in such a way as to contain sub-monolayer quantities of Te (so-called delta-doped ZnSe:Te), exhibits optical properties consistent with the presence of quantum size centers. We present results of excitation intensity and temperature dependent cw photoluminescence (PL) as well as time-resolved PL measurements that explicitly show that the ensemble of type-II quantum islands is formed in this system. Specifically, for the 2.46–2.51 eV PL we show that (1) its maximum shifts as a cube root of excitation intensity; (2) its full-width-at-half-maximum decreases with the temperature while its maximum undergoes a red shift in the temperature interval where the integrated PL intensity stays approximately constant; (3) the PL decay is non-exponential at high excitation intensities and a single exponential decay at low excitation intensities; (4) the PL life-time initially increases with temperature from of 86 ns at T = 15 K to 143 ns at T = 115 K before deceasing due to non-radiative processes.

1 Introduction Zn–Se–Te system has long been of interest because of its interesting optical properties. Many studies on both bulk and molecular beam epitaxy (MBE) grown $ZnSe_{1-x}Te_x$ have been performed to understand the system (see Ref. [1] and references therein). It is generally agreed that the dominant photoluminescence (PL) from $ZnSe_{1-x}Te_x$ alloys is due to excitons bound to various Te related defects. Specifically, two PL band are often observed: a band at ~2.65 eV ("blue band") that usually dominates at small Te concentrations (up to $x < 0.015$) and a band at ~2.45–2.50 eV ("green band") dominates in samples with larger x (see e.g., Refs. [1, 2] and references therein). Akimova et al. [3] used cathodoluminescence to obtain the most direct evidence that the 2.65 eV band is due to Te_2 and that the 2.45–2.48 eV band is predominantly due to Te_3 complexes, respectively. The similar PL is also observed in low dimensional ZnTe/ZnSe structures (see e.g. Ref. [4]), and it is generally attributed to Te_n cluster isoelectronic bound excitons (IBE) too.

In this paper we re-visit discussion of the PL from a so-called triple-delta-doped Zn–Se–Te system (denoted further as δ^3-ZnSe:Te). It is obtained by depositing sub-monolayer quantities of Te, without a Zn flux present, on Zn terminated ZnSe layers that behave as spacers during MBE growth (the details are given elsewhere [1]). It will be important for further discussion, that no full ZnTe monolayers are formed in such a structure as confirmed by reflection high-energy-electron diffraction and transmission electron microscopy (TEM) [5] and that the average over the sample Te concentrations do not exceed ~1.8% as confirmed by x-ray diffraction [1] and secondary ion-mass spectroscopy [5]. Thus, we shall show by

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more detailed investigation of cw PL and by means of time-resolved PL (TRPL) that the green band in δ^3-ZnSe:Te is due to centers characterized by quantum confinement effects.

2 CW photoluminescence In Fig. 1(a), we reproduce the full-width-at-half-maximum (FWHM) of the green band from Kuskovsky et al. [1]. It stays constant up to $T = 80$ K and then decreases until $T \sim 120$ K by as much as 35 meV, where it starts increasing again. The observed narrowing of the PL width is in contrast to what has been observed from a green band in ZnSeTe alloy [6], where the FWHM increased almost monotonically with increasing temperature. We have already attributed the decrease in FWHM to the presence of the ensemble of the centers characterised by various localization energies [1]. Furthermore, in the same temperature region the green band energy peak position undergoes a red shift by as much as 25 meV (Fig. 1(b)) relative to the ZnSe bandgap while its integrated PL intensity stays relatively constant (Fig. 1(c)). We are not aware of any report on such behavior in any system with IBEs. However, these features of temperature dependent PL are routinely observed for the quantum dot (QD) ensemble in various material systems: GaSb/GaAs [7], InP/GaAs [8], InAs/GaAs [9], CdTe/ZnTe [10], and CdSe/ZnSe [11].

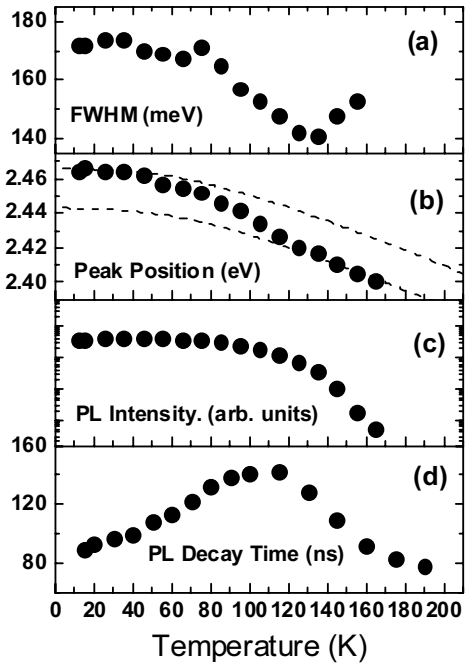

Fig. 1 (a) FWHM; (b) peak position; (c) integrated intensity; (d) time decay constant as functions of temperature; the dashed line is the ZnSe bandgap shown to guide the eye.

To further understand the origin of these centers, we have re-evaluated the excitation intensity dependent PL. Using a Gaussian fit, we have found that the peak position of the present green band shifts with the excitation intensity by as much as 31 meV (Fig. 2) in a given experimental setup; we note that using a Xe lamp for weak excitation and a laser for strong excitation, we estimate that the green band maximum could shift as much as 45 meV. At the same time the blue band shifts less than 9meV. Therefore, such a large shift of the green band cannot be explained by overlap with the blue band, since in this case both bands should exhibit comparable shifts. Moreover, the peak shift as a function of excitation intensity is not expected for IBEs either. However, this is easily understood if one considers quantum structures with a type-II band alignment [12, 13].

Therefore, since ZnTe/ZnSe heterostructures are type-II (with holes strongly confined by a large potential of ~0.8–1.0 eV within ZnTe and electrons weakly confined within ZnSe), we suggest that ZnTe-rich QD-like centers are indeed formed in δ^3-ZnSe:Te, and that they are responsible, for the most part, for the ~2.46–2.51 eV PL band. This is also confirmed by the fact that the peak position is almost a linear function of cube root of the normalized excitation intensity (see dashed line in Fig. 2), which is often observed for type-II quantum structures [13].

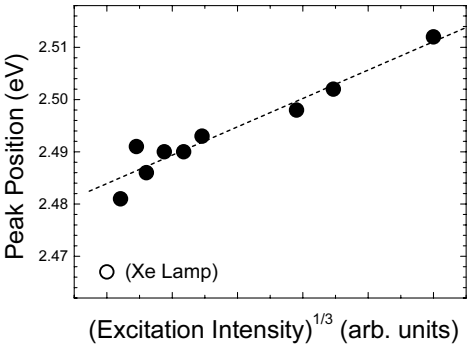

Fig. 2 The peak position vs cube root of excitation intensity; the dashed line is a linear fit. The open circle is the peak position under "weak" lamp excitation (intensity is not shown to scale)

3 Time-resolved photoluminescence To further support our conclusions we performed time-resolved PL measurements. The results are shown in Fig. 3. The observed PL decay is non-exponential at high excitation intensities,

approaching a single exponential function under lower excitations. Moreover, the long-time tails of the high excitation intensity curves are parallel to the single exponential decay obtained at low excitation intensities.

These observations are easily understood within a model of type-II nanostructures. Indeed, in type-II heterostructures the photo-generated carriers create an electrical field that leads to the band bending, the magnitude of which depends on the carrier concentration [13]. At very high carrier concentrations (strong excitation) the band bending results in the strong overlap of electron and hole wave-functions and, therefore, in a faster decay. As time elapses, and the carrier concentrations decrease, the wave-function overlap becomes weaker and the decay becomes slower [14], approaching the case of the "flat" bands. The same decay, obviously, should be observed under weak excitation conditions when the concentration of photo-generated carriers is low (Fig. 3, the lowest curve). Thus, in our further discussions we take the decay time obtained at the lowest excitation intensity as the characteristic lifetime of electron–hole pairs in our system.

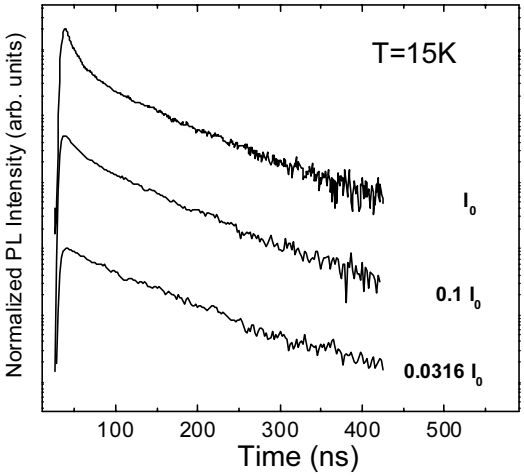

Fig. 3 Time-resolved PL for the green band at 2.46eV obtain at several excitation intensities.

It must be noted that the decay is expected to be slower in systems with quantum confinement [15], and even more so in type-II structures due to the spatially indirect nature of the electron-hole recombination. We have indeed observed an increase in the decay times compared with alloys. Akimova *et al.* [3] have reported the decay time of 35 ns (at 77 K) for the green band in the $ZnSe_{0.98}Te_{0.02}$ alloy. This is significantly lower than 132ns obtained from δ^3-ZnSe:Te at 80 K (Fig. 1(d)); note that this is also lower than 86ns obtained at 15K. Such a discrepancy strongly indicates a different origin of the green band in bulk alloy and in δ^3-ZnSe:Te, and as well it supports our conclusions about the presence of type-II quantum structures.

The increase of the green PL lifetime as a function of temperature (Fig. 1(d)) is consistent with the presence of type-II quantum islands as well. Two mechanisms might be responsible for the increase in the lifetime with increasing temperature (the decrease at $T > 120$ K is due to non-radiative processes). On the one hand, such a behavior has been predicted for either large QDs [15] or quantum islands [16] (note that there are no QWs present in our system). On the other hand, however, since our structures are type-II we suggest that another mechanism is predominantly responsible for the observed temperature dependence of the PL lifetime. As the temperature rises, the weakly bound electrons are ionized, while strongly confined holes are still trapped within nano-islands. As a result, the electrons are away from the holes for a relatively long time before being re-captured with the subsequent radiative recombination, which leads to the longer PL lifetime. This explanation is valid only if the non-radiative processes are negligible. We emphasize that this condition is indeed fulfilled in our case as the PL intensity is relatively constant within the temperature interval of interest (compare Figs. 1-(c) and 1-(d)). More detailed and quantitative discussion is presented elsewhere [17].

4 Conclusions In conclusions, we have shown using excitation intensity and temperature dependent cw and time-resolved photoluminescence that the so-called green band observed in photoluminescence of triple-delta-doped ZnSe:Te is due to excitons formed in type-II quantum islands.

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