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Time-resolved photoluminescence of type-II quantum dots and isoelectronic centers in Zn–Se–Te superlattice structures

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Spectrally and time-resolved photoluminescence of a ZnTe/ZnSe superlattice reveals a smooth transition of the photoluminescence (PL) lifetime from ~100 ns at 2.35 eV to less than a few nanoseconds at 2.8 eV. The significant increase of the lifetime in the low energy region is strong evidence to support the formation of type-II quantum dots (QDs), since in these nanostructures the spatial separation of carriers is increased. The shorter lived emission above 2.5 eV is attributed to excitons bound to Te isoelectronic centers in the ZnSe matrix. The smooth transition of the PL lifetime confirms that clusters of these Te atoms evolve into type-II ZnTe/ZnSe QDs. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2835699]

Recently, $ZnSe_{1-x}Te_x$ dilute alloys $(x \leqslant 4\%)$ have been under extensive investigation due to their interesting optical properties.[1–4] For example, autocorrelation experiments have shown that isoelectronic centers (ICs) (Refs. 2 and 3) formed by two or more excitons bound to Te atoms can emit single photons.[5] This may be interesting for quantum cryptography applications. Also, ZnTe/ZnSe multiple quantum well (MQW) and superlattice structures have been grown in hope of achieving tunable optical properties via quantum confinement effects (e.g., Ref. 6). However, the photoluminescence (PL) of these structures is heavily dominated by IC emission, and explicit experimental evidence of the PL emission from quantum confined excitons was not observed until recently.[7]

The structure in Ref. 7 that shows evidence of quantum confinement is an epitaxially grown Zn–Se–Te multilayer system with a 240 period ZnTe/ZnSe superlattice structure. During the layer-by-layer growth, Te atoms are introduced in submonolayer quantities, by migration enhanced epitaxy.[4] Despite the intention to build a superlattice, transmission electron microscopy showed no evidence of quantum well formation.[8] Nevertheless, the PL of this structure exhibits strong evidence of the formation of ZnTe/ZnSe quantum dots (QDs) with a type-II band alignment.

Type-II QDs have attracted considerable attention since they have been predicted to exhibit the Aharanov–Bohm effect for neutral particles.[9] Unfortunately, the PL of the QDs in the Zn–Se–Te systems is convoluted with the luminescence of excitons bound to ICs ($Te_{n\geqslant 2}$) within the so called "green band."[7] Moreover, PL studies indicate that there is a smooth transition in the electronic properties from ICs to type-II QDs,[7] so the clear distinction between IC and QDs is of high interest. In this letter, we present spectrally and time-resolved photoluminescence (TRPL) results of this ZnSe:Te multilayer system. Furthermore, a full spectrum analysis of the PL decay clearly confirms the evolution of the Te ICs into type-II ZnTe/ZnSe quantum dots (QDs).

To help us in the TRPL analysis, the PL was reexamined in more detail. Figure 1 shows the PL at $T=4$ K, excited with a HeCd laser at 3.81 eV. This PL is dominated by the emission of two well resolved bands, which is consistent with previous results for this system.[3,4] The higher energy band ("blue band") between 2.6 and 2.75 eV is generally accepted to be the result of emission from the contribution of numerous Te_2 complexes (region A), while the lower energy green band at ~2.5 eV (region B) has been traditionally attributed to the emission from $Te_{n\geqslant 2}$ clusters, and more recently to an admixture of such $Te_{n\geqslant 2}$ complexes and type-II QDs (B).[7,10] To analyze the spectrum, we have deconvolved the luminescence into Gaussian peaks (see inset of Fig. 1), since both blue and green bands are to be broadened inhomogeneously due to the random spatial distribution of the Te_2 complexes, and the random spatial and size distributions of the $Te_{n\geqslant 2}$ complexes and type-II QDs. It is important that a third peak

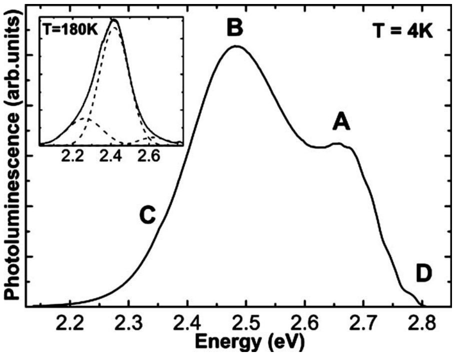

FIG. 1. cw PL at 4 K. The PL can be deconvolved into three peaks, one for the blue band (A), one for the green band (B), and one for the large size QDs (C). The free excitons in the Zn(Te)Se matrix are also evident (D). The inset shows the PL and 180 K with an example of the Gaussian deconvolution of the emission.

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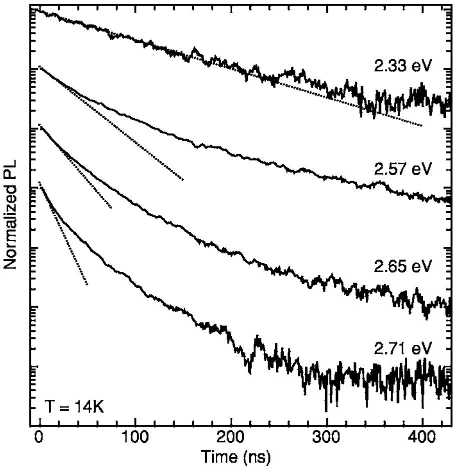

FIG. 2. PL decay near the tail of the green band (2.33 eV), the peak of the green band (2.57 eV), the peak of the blue band (2.67 eV), and the side of the blue band (2.71 eV). Each one of the dotted lines are the best exponential decay that can represent initial decay.

in the tail of the green band (<2.3 eV) is required to complete the deconvolution. It must be noted that magneto- and temperature dependent PLs indicate that this feature, which can be observed as a weak shoulder (region C) in Fig. 1, and is much more clearly seen at 180 K (see inset), is the result of larger Te-rich ZnTe QDs.[11] The existence of these purely type-II QDs in the low energy tail of the green band emission is confirmed by TRPL. Finally, a small feature at ~2.79 eV (region D) is also evident in Fig. 1; we attribute it to free excitons in the Zn–Te–Se matrix (see also absorption measurements in Ref. 7).

TRPL was conducted using an ultrafast laser system (Coherent Mira-RegA) for excitation and a streak camera system for detection. Frequency tripling was used to upconvert the 800 nm laser output to 266 nm for excitation. The sample was placed inside a cryostat cooled by closed cycle refrigeration to 14 K. The PL was spectrally resolved by a Chomex 250IS spectrograph, and temporally analyzed by a Hamamatsu C4334 streak camera.

Figure 2 shows the PL decay from four different regions on the spectrum at 14 K. As expected, the decay from the regions within the green band are longer than that from the regions within the blue band, a direct result of the spatial separation of the charged particles in the type-II QDs. Another interesting result is the evolution of the decay from a single exponential (as expected at low pump power[7]) in the low energy tail in the green band to nonexponential in the high energy side in the blue band. Such a non-exponential PL decay has been observed previously in a similar single ZnSeTe structure, and was attributed to the contribution of dark excitons to the PL lifetime.[5] However, the temperature dependence of the non-exponential PL decay described in Ref. 5 was not observed in the ZnSeTe multilayer structure discussed here. therefore, although this explanation cannot be totally discounted, we believe that the non-exponential behavior observed in Fig. 2 is the result of a different mechanism.

An alternate explanation of the nonexponential decay characteristics is a layer-by-layer evolution caused by strain relaxation, whereby the system evolves from highly strained layers that contain only ICs, to less strained layers containing both ICs and type-II QDs, and finally to layers with low strain consisting of predominately type-II QDs near the surface. In the layers of ICs and ICs with QDs, complex carrier dynamics can occur, through which thermalized carriers can transport to other types of recombination centers before recombining. The redistribution of carriers in a system with different types of recombination centers can often lead to a nonexponential PL decay, e.g., as typically seen in In-segregated InGaN,[12–14] amorphous silicon,[15,16] and heavily doped semiconductors.[17]

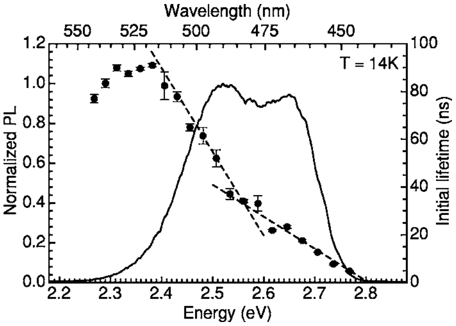

FIG. 3. Initial PL decay lifetime for every 5 nm over the background of time integrated PL. The dashed lines indicate the decrease of lifetime per unit energy in the green band and the blue band.

To compare the PL decay from one end of the spectrum to the other quantitatively, we have plotted the initial PL decay lifetime for every 5 nm throughout the spectrum (see Fig. 3), by approximating the initial decay by an exponential. The maximum of the PL lifetime occurs around 2.35 eV, which interestingly coincides with the emission attributed to ZnTe QDs in the tail of the green band. Since the charge separation due to type-II band alignment prolongs the PL lifetime of the QDs, and the lifetime maximum occurs at 2.35 eV, it follows that the luminescence at 2.35 eV (C) can be unambiguously attributed to a type-II transition between the ZnSe conduction band and the ZnTe valence band associated with the larger ZnTe/ZnSe type-II QDs.

From this PL lifetime maximum on the high energy side of the spectrum, the PL lifetime monotonically decreases. This decrease extends continuously into the blue band, which indicates that a smooth transition occurs from QDs to ICs. However, there is a greater change of lifetime per unit energy between 2.4 and 2.55 eV than between 2.55 and 2.80 eV, which clearly marks a difference between the green band and the blue band (see Fig. 3).

In the blue band, the short PL lifetime reflects the direct excitonic nature of the emission in this spectral range. However, the increase of the PL lifetime across the blue band toward lower energy suggests an increased contribution of the type-II QDs, whose inhomogeneous distribution overlaps that of the ICs. This is illustrated further in Fig. 2 where the fast initial lifetime of the high energy emission (>2.5 eV) rests upon a longer lived background, the size of which increases relative to the PL lifetime of the IC complexes for lower PL energies.

In the green band, the relative contribution of the type-II QDs increases and eventually dominates the emission on the low energy side of the spectrum. Since the contribution of the ICs is a minority process in this spectral regime, changes in the PL lifetime simply reflect the inhomogeneous broadening of the type-II QDs. The increased contribution of type-II QDs in the green band is supported by the increasingly long lived PL lifetime at energies below 2.5 eV in Fig. 2.

Finally, the slight decrease in the PL lifetime on the lower energy tail (<2.35 eV) requires further study. We tentatively attribute this behavior to impurities or defect states formed on the QD surface, the origin of which although unclear, may be related to the strain relaxation of larger QDs due to strain interaction of the coupled QD layers. This is known to increase dislocation and defect formation significantly in InAs QDs.[18] Such dislocations and defects would significantly decrease the PL lifetime of the QDs due to an increased contribution of nonradiative processes.

In summary, we have studied the TRPL of a 250 periods ZnTe/ZnSe superlattice structure, which shows strong evidence of ZnTe/ZnSe QD formation. The evolution of the PL characteristics from one end to the other end of the spectrum indicates that there is a layer-by-layer evolution of material. Furthermore, the continual monotonic decrease in the PL lifetime from the low energy tail of the green band to the high energy side of the blue band strongly indicates a smooth transition of this evolution from IC rich layers to QD rich layers.

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