

Zn-Se-Te multilayers with submonolayer quantities of Te: Type-II quantum structures and isoelectronic centers

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(Received 13 July 2004; published 31 January 2005)

Detailed studies with spectral and time-resolved photoluminescence, photoluminescence excitation, and absorption spectroscopies show the formation of type-II quantum structures (quantum dots) in a Zn-Se-Te multilayer system with submonolayer quantities of Te. Moreover, it is shown that in addition to these quantum dots, Te isoelectronic centers are also present in the same material system and contribute to the photoluminescence emissions. This could be significant for the better understanding of the scaling laws between many-atom systems (e.g., quantum dots) and few-atom systems (e.g., isoelectronic centers).

DOI: 10.1103/PhysRevB.71.045340

PACS number(s): 78.67.Pt, 71.55.-i, 78.66.Hf

ZnSe_{1-x}Te_x diluted alloys ($x \leq 4\%$) have been under extensive investigations for their interesting optical properties. The photoluminescence (PL) of these alloys is usually attributed to excitons bound to isoelectronic centers (ICs). The centers that dominate the optical properties are so-called Te₂ and Te_{n≥3} ICs (see, e.g. Refs. 1–3), where two and three or more Te atoms are bound to the same Zn atom.

More recently, ZnTe/ZnSe multiple quantum well (QW) and superlattice structures have been obtained in the hope of achieving tunable optical properties by taking advantage of quantum confinement effects. However, the PL of these structures always have been attributed to isoelectronic bound excitons (see, e.g., Ref. 4) instead of quantum-confined excitons. Although ZnTe/ZnSe quantum dots (QDs) have been grown and the PL was suggested to originate from these QDs,⁵ no explicit supporting experimental evidence and detailed studies were provided.

Here, with an epitaxially grown Zn-Se-Te multilayer system with submonolayer quantities of Te, namely δ^3 -ZnSe:Te (for this specific growth method and the sample structure, see Ref. 3), for which no QW structures were found by transmission electron microscopy,⁶ we, for the first time, explicitly prove the existence of ZnTe/ZnSe QDs. These QDs, as expected,⁷ have a type II band alignment as shown by detailed PL studies. Additionally, we show that in this Zn-Se-Te system, the isoelectronic centers coexist with type II QDs and also contribute to the PL emissions. This coexistence might provide an ideal platform to gain further insight into the evolution from few-atom systems (e.g., ICs) to many-atom systems (e.g., QDs). For instance, a rather smooth transition in electronic properties from ICs to QDs has been suggested for the In-Ga-N system by calculations,⁸ but no experimental studies are available.

The PL (obtained at $T=10$ K) of δ^3 -ZnSe:Te is plotted in the inset to Fig. 1, and consists of two broad bands similar to those observed from ZnSe_{1-x}Te_x alloys with $x \geq 0.016$ (see, e.g., Ref. 2). Previously,³ the “high” energy band (“blue band”) and the “low” energy band (“green band”) were attributed to excitons bound to Te₂ and Te_{n≥3} complexes, respectively. We shall here first show, by use of the excitation intensity and temperature dependent and time-resolved PL,

that the green band of δ^3 -ZnSe:Te contains contributions from type II QDs. We shall subsequently show, by use of the photoluminescence excitation (PLE) and absorption spectroscopies, that, in addition, the green band also contains contributions from ICs. The peak positions of the green band (green solid circles) and the blue band (blue open circles) are plotted in Fig. 1 as functions of excitation intensity. A very careful analysis of the PL peak positions at various excitation intensities⁹ shows that while the blue band exhibits very little shift, the green band shifts more than 31 meV over four orders of magnitude of change of excitation intensity. Moreover, the shift of the green band can be as much as 45 meV (not shown here), if a Xe lamp is used as a source of weak excitation and a laser is used to achieve high excitation intensities. Such a large shift cannot be explained either by the overlap of the green and blue bands (in this case the shifts of both bands should be comparable) or by excitons bound to ICs, for which no shift is expected. On the other hand, this

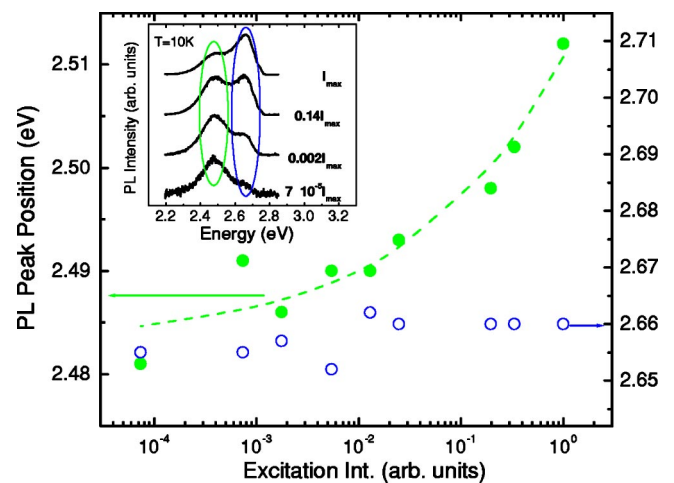


FIG. 1. (Color online) The semilogarithmic plot of the green PL peak (the region marked in green in the inset) position (green solid circles) and the blue PL peak (the region marked in blue in the inset) position (blue open circles) at $T=10$ K as a function of excitation intensity (I_{ex}) for δ^3 -ZnSe:Te. The dashed line is the result of fitting with $I_{\text{ex}}^{1/3}$.

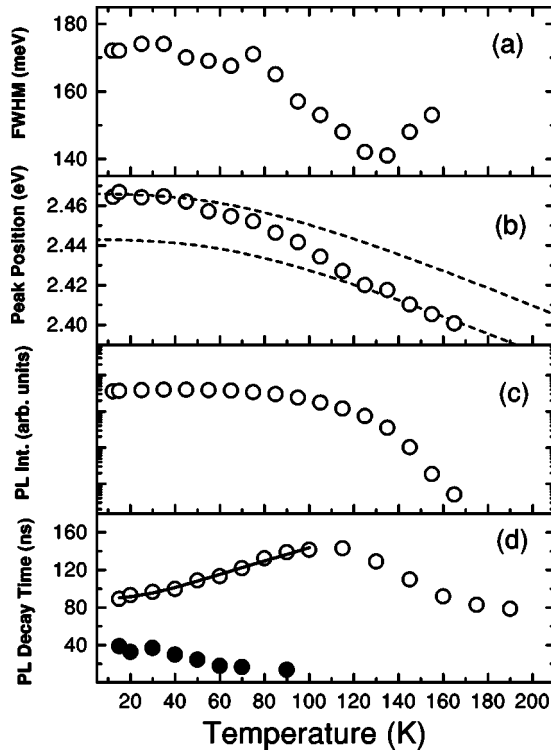


FIG. 2. (a) The FWHM, (b) the PL peak position (open circles), (c) the integrated PL intensity, and (d) the PL decay time (open circles) of the green band of δ^3 -ZnSe:Te as functions of temperature. Also, for comparison, the ZnSe band-gap temperature dependence (dashed lines) and the blue band PL decay time (solid circles) of δ^3 -ZnSe:Te are plotted in (b) and (d), respectively. The solid line in (d) is the fitting result using Eq. (1).

type of behavior is routinely observed for type II QWs¹⁰ and type II QDs^{11,12} due to the dependence of energy levels on the excitation intensity.^{10,11} Moreover, the peak position here follows the cube root of the excitation intensity (the green dashed line in Fig. 1), which is predicted for type II nanostructures.¹⁰

Next, in Figs. 2(a)–2(c) we plot, for the same sample, the temperature dependence of the full width at half maximum (FWHM), the peak position and the integrated intensity of the green band, respectively. The FWHM stays constant up to $T=80$ K and then decreases until $T=120$ K by as much as 35 meV, where it starts increasing. The peak energy undergoes a redshift (with increasing T), by as much as 25 meV, relative to the ZnSe bandgap in the temperature region where the narrowing of the linewidth is observed. Such a narrowing of the linewidth is in contrast to an increase in the FWHM observed from a similar green band (whose origin is due to excitons bound to Te_3 ICs¹) in ZnSeTe alloys.¹³ We note that the concurrence of the band narrowing and the redshift of the peak position is typical for an ensemble of QDs,^{14–19} which is explained by exciton transfer between QDs.¹⁴ Therefore, we attribute this behavior to the existence of multiple centers associated with Te, including QDs. Also, within the same temperature region, the integrated PL intensity remains almost constant; the significance of this observation will be discussed below, in connection with Eq. (1).

The existence of type II QDs is further supported by time-

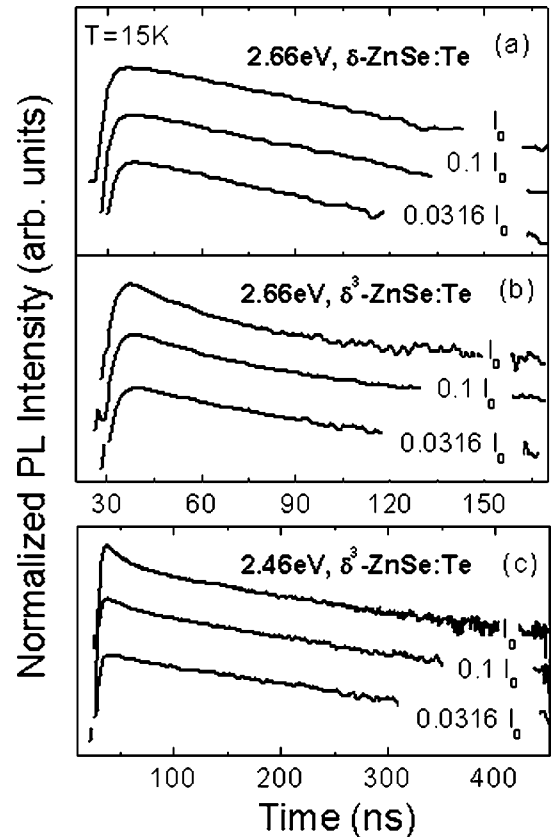


FIG. 3. The decay of the (a) the blue band of δ^3 -ZnSe:Te, (b) the blue band of δ^3 -ZnSe:Te, and (c) the green band of δ^3 -ZnSe:Te at various excitation intensities at $T=15$ K plotted in a semilogarithmic scale; the detection energies are given in the graphs.

resolved PL results. The low temperature ($T=15$ K) PL decays, for the δ^3 -ZnSe:Te sample, of the blue band (detected at 2.66 eV) and of the green band (detected at 2.46 eV), obtained under various excitation intensities, are plotted in Figs. 3(b) and 3(c), respectively. The same data (detected at 2.66 eV) from a δ -ZnSe:Te sample (for notations and sample description see Ref. 3) are also shown, for comparison, in Fig. 3(a). It is obvious that under the lowest excitation intensity all the PL curves exhibit a single exponential decay, from which a characteristic decay time (τ_g for the green band and τ_b for the blue band) can be obtained (the decay behavior under strong excitations will be discussed below). We obtain $\tau_g \approx 86$ ns, and for the blue bands of δ -ZnSe:Te and δ^3 -ZnSe:Te, we obtain $\tau_b \approx 30$ and 38 ns, respectively. Note that $\tau_b \approx 16$ ns at $T=70$ K [solid circles in Fig. 2(d)] is close to the decay time of ~ 20 ns obtained at $T=77$ K for the blue band in bulk ZnSeTe alloys.¹ As to the green band, there is a large discrepancy with results between δ^3 -ZnSe:Te and bulk ZnSeTe alloys, with $\tau_g \approx 122$ ns obtained at $T=70$ K [open circles in Fig. 2(d)] being much larger than that of alloys, which is ~ 35 – 40 ns obtained at $T=77$ K.¹ Thus, we conclude that, while the blue bands from both our samples (δ -ZnSe:Te and δ^3 -ZnSe:Te) and alloys are due to the same origin (excitons bound to Te_2 ICs), the origin of the green band PL in δ^3 -ZnSe:Te and alloys is

different. Such a difference is to be expected if there is formation of type II QDs, since excitons localized in this type of structure have longer lifetimes due to the weak overlap of electron and hole wavefunctions.¹² Moreover, as can be seen from the temperature behavior of τ for both bands (δ^3 -ZnSe:Te), plotted in Fig. 2(d), the green band PL decay time even increases with increasing temperature up to $T = 115$ K, while the blue band PL decay time decreases monotonically.

An increase in τ can be readily understood for type II QDs, as the temperature rises, the weakly bound electrons are ionized, and, as a result, are away from the strongly localized (confined) 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, which is confirmed by the almost constant PL intensity in the same temperature region [Fig. 2(c)]. Interestingly, this type of behavior was also observed for certain systems with ICs (ZnTe:O²⁰ and GaAs_{1-x}P_x:N for some x values²¹) due to a similar effect. In Ref. 20, the temperature dependence of τ was fitted with the formula

$$\tau = \tau^* / [1 - C \exp(-\varepsilon/kT)], \quad (1)$$

where τ^* is the decay time at $T=0$ K, C is a constant, ε is a characteristic energy that is of the order of the electron-hole (e - h) binding energy, and k is the Boltzmann constant. Following Ref. 20, we fit τ_g using Eq. (1). In Fig. 2(d) the solid line is the fitting result within the temperature region where the PL intensity remains relatively constant [Fig. 2(c)], i.e., where nonradiative processes are negligible, and it yields $\varepsilon \approx 7$ meV, which is significantly lower than the free exciton binding energy in either ZnSe (~ 20 meV²²) or ZnTe (~ 13 meV²²). Such a low e - h binding energy is indeed expected for type II QDs due to the spatial separation of electrons and holes.²³

Regarding the PL decay behavior under high excitation intensities, this is a nonexponential; this type of decay has been observed for type II QDs,¹² and is explained by the change of the overlap of electron and hole wave functions as a function of time. In type II QDs the overlap of the wave functions depends on the band bending;¹² this, in turn, depends on the photogenerated carrier concentrations,^{10,12} which of course decreases over time. Thus one would expect that under low excitation intensities or after a long time, the overlap of the wave functions approaches a constant, and consequently that the decay will become a single exponential, which we indeed have observed for the green band [Fig. 3(c)]. We note that the blue band of δ -ZnSe:Te [Fig. 3(a)] does not show any nonexponential decay, as expected for excitons bound to ICs.

Having established the existence of type II QDs in δ^3 -ZnSe:Te, we next show (using the absorption and PLE spectroscopies) that they co-exist with Te_n ICs. The absorption and PLE spectra are shown in Fig. 4. Both exhibit a similar, relatively broad peak around 2.789 eV, with the absorption spectrum showing an additional, sharp, peak around 2.802 eV that we attribute to the free exciton (FX) in the ZnSe buffer region.²⁴ We attribute the 2.789 eV peak to the

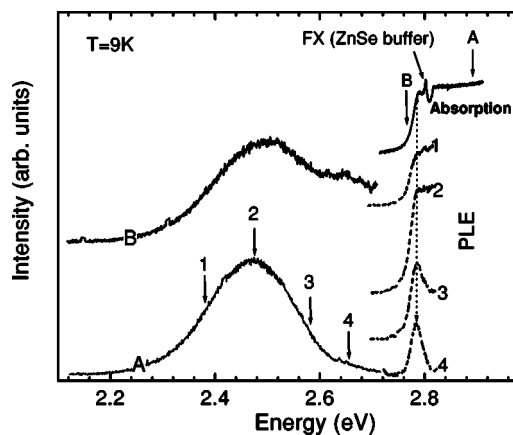


FIG. 4. The absorption, PLE and PL spectra of δ^3 -ZnSe:Te at $T=10$ K. The PLE detection energies are indicated by the arrows (1, 2, 3, 4) across the PL spectrum. PL curve A is obtained with an above-band-gap photon energy excitation (indicated by arrow A), and PL curve B is obtained with excitation (indicated by arrow B) into the low energy tail of the absorption spectrum.

free exciton from the spacer regions (ZnSe), whose energy is modified by the presence of Te due to some, minimal, Te diffusion (using the formula given in Refs. 25–27, we estimated the Te concentration to be between 0.4% and 0.7%).

From the PLE detected at various energies across the PL spectrum (indicated by arrows 1, 2, 3, and 4) it is clear that the blue band energy region (arrow 4) as well as the high energy part of the green band (arrow 3) are preferentially excited via the free exciton from the spacer regions, whereas the low energy part (arrow 1) and the peak (arrow 2) of the green band are preferentially excited via band-to-band processes. Furthermore, for excitation with an energy in the tail of the absorption edge, the PL (curve B) shows an enhanced blue band and high energy part of the green band, compared to excitation with above-band-gap energy (curve A).

To understand these results, we note that in ZnSeTe alloys, under the same excitation condition as that used to obtain curve B, the whole green band was enhanced;¹³ therefore, it is obvious that the present green PL must have (at least) two different origins, one giving the low energy part, and one giving the high-energy part. Furthermore, there are striking similarities in the PLE curves for our blue band as well as the high energy side of our green band, and the PLE from alloys.^{13,28} Therefore, we attribute the high energy part of our green band to excitons bound to ICs, and the low energy part of the green band to excitons associated with type II QDs. Indeed, the PL due to excitons bound to ICs is enhanced under excitation by free excitons, due to direct capture by the ICs; on the other hand, because of the spatially indirect nature of excitons associated with type II QDs (spatially direct excitons cannot be directly captured by type II QDs), the PL is strongly favored by the band-to-band excitation, where free carriers are generated.

Thus, PLE can be used to probe the formation of spatially indirect excitons; such excitons are directly linked to the formation of type II QD band structures (energy barriers). As can be seen from Fig. 4, the free exciton peak at 2.789 eV

(spatially direct exciton) on the PLE curve gradually disappears as the band-to-band excitation starts to dominate; this indicates that there is a smooth switch to PL from spatially indirect excitons with the change in detection energy (of the green band). This, in turn, suggests the smooth transition from ICs to type II QDs.

In summary, we have shown that there is a formation of QDs in Zn-Se-Te multilayers. The PL properties of these QDs are characteristic of spatially indirect excitons, as ex-

pected for type II quantum structures. Furthermore, the Te isoelectronic centers are shown to coexist with type II QDs in the same sample, and a smooth transition between these two different centers is indicated by experimental results. This might be significant for understanding the scaling laws from many-atom systems (e.g., QDs) down to few-atom systems (e.g., ICs). We hope this work can stimulate theoretical calculations on the formation of QDs out of few-atom systems such as isoelectronic centers.

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