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Optical investigations of the influence of point defects on quantum dots in CdSe/ZnSe heterostructures

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Abstract

Optical properties of single-layer and multistack CdSe/ZnSe self-assembled quantum dot (QD) heterostructures have been investigated. It is found that QDs at the interface can accumulate cation vacancy-related defects. In this case the level of defects is associated with the quantized heavy-hole level of the QDs. It is shown that study of the excitation spectra of the defect-related band enables one to obtain information about optical transitions in QDs.

1. Introduction

Optical properties of CdSe/ZnSe self-assembled quantum dot (QD) structures have been intensively investigated during recent years because of their possible application, in particular, in blue–green lasers with low threshold current [1]. However, it is obvious that the intensity and stability of the emission of such structures will depend on the density of point defects. The presence of such defects in heterostructures can be caused both by deviations from the stoichiometric composition during the growth processes and by impurity diffusion from the substrate. The final distribution of defects inside the structure can be significantly influenced by heterointerfaces. In particular, the QD/barrier (wetting) layer interface can serve as a sink for point defects. The presence of stress/strain features caused by lattice mismatch between the QD and barrier (wetting) layers could also stimulate a process of point defect gettering. In the present paper the local arrangement of point defects in CdSe/ZnSe heterostructures with QDs has been investigated by optical methods.

2. Experiment and results

Two series of structures grown by MBE on (100) GaAs substrates have been studied:

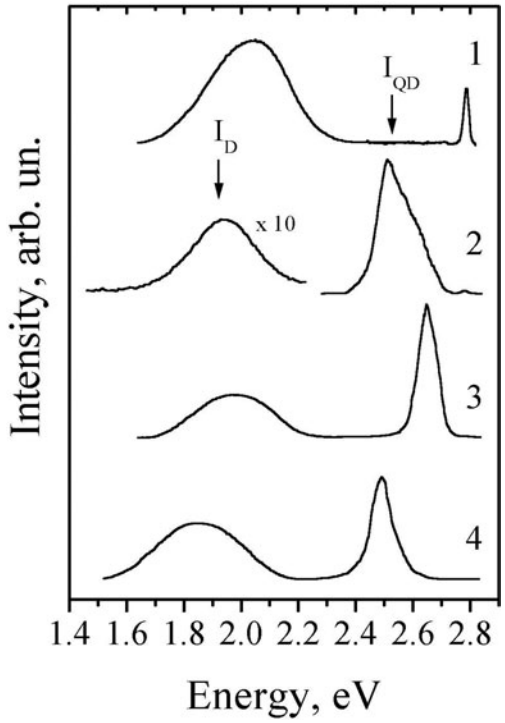

Figure 1. PL spectra of a ZnSe epilayer (curve 1) and CdSe/ZnSe heterostructures with a single CdSe layer of nominal thickness 3.5 ML (curve 2) and 12 vertically stacked CdSe layers of nominal thickness 2.1 ML (curve 3) and 3.5 ML (curve 4). $T = 77$ K.

(i) structures with a single Cd-rich layer obtained by deposition of 3–5 ML (monolayers) of CdSe,

(ii) structures with 12 vertically stacked CdSe layers of 2.1–3.5 ML nominal thickness separated by ∼18 nm ZnSe spacers.

All the structures were grown on a 200 nm thick ZnSe buffer layer and capped by a 100 nm ZnSe layer. The ZnSe buffer and ZnSe barriers were grown at 280 and 230 °C, respectively. After the deposition of each CdSe layer the Cd beam was blocked and the structure was heated up to 340 °C and then cooled down to 230 °C under Se flux. The duration of the last two steps was 4 min. After such a procedure a ZnSe barrier or top layer was grown. The RHEED method was used for *in situ* control of three-dimensional island formation. The single-layer samples were grown at a VI/II group beam pressure ratio of 3:1 while the multistack samples were grown at a 5:1 ratio. For comparison, nominally undoped 0.6 μmm thick ZnSe films were studied too.

The photoluminescence (PL) spectra were measured in the temperature range 4.2–300 K. PL was excited by the discrete lines of an Ar^+ or N_2 laser. Cathodoluminescence (CL) measurements were carried out at 77 and 300 K in scanning mode using an electron beam with primary energy 20 keV and beam current up to 350 μA (spot size: 20–30 μm). Photoluminescence excitation (PLE) spectra were measured at 4.2–77 K using a glow lamp source.

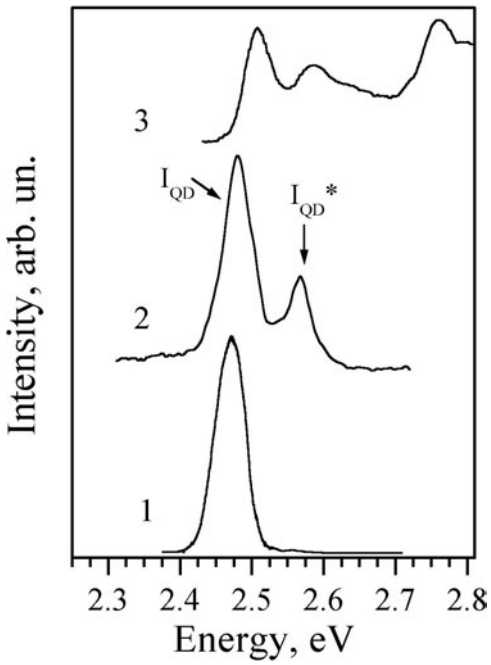

Figure 2. PL (curve 1), cathodoluminescence (curve 2) and I_D band excitation (curve 3) spectra of CdSe/ZnSe heterostructures with 12 vertically stacked CdSe layers of nominal thickness 3.5 ML. $T = 77$ K.

The PL spectra at 77 K for all CdSe/ZnSe structures investigated consist of two emission bands: I_{QD} at 2.33–2.69 eV with FWHM 28–115 meV and the broad band I_D with a maximum at 1.82–1.99 eV for different samples (figure 1, curves 2–4). Increase of the nominal thickness of the CdSe layer in single-layer and multistack samples leads to the shift of both I_{QD} and I_D band maximum positions to the low-energy region of the spectra (figure 1, curves 3, 4).

With the increase of the photoexcitation power the I_{QD} band maximum position shifts gradually towards the high-energy region and its halfwidth increases. At high excitation levels an additional maximum I^*_{QD} appears on the high-energy side of the I_{QD} band (figure 2, curve 2). The energy distance between the I_{QD} and I^*_{QD} band maxima in the CL spectra increased with the shift of the I_{QD} band to the low-energy region and was 30–100 meV at 77 K for different samples.

The characteristics of the I_{QD} and I^*_{QD} bands described above are in agreement with previously reported results on structures grown by similar methods [2, 3]. Such bands were respectively interpreted as radiative recombinations of ground-state heavy-hole-like (e–hh) and light-hole-like (e–lh) exciton transitions in QDs [4]. It should be noted that for both e–hh and e–lh transitions, a Stokes shift of up to 25 meV was observed between the positions of the corresponding maxima in luminescence and PLE spectra.

The I_D band maximum position shifts to the high-energy region with the increase of the QD emission energy. For multistack samples at $T = 77$ K, the I_D band maximum position depends linearly on the I_{QD} band maximum position, i.e. on the energy gap between the ground electron and hole levels in QD. The slope of this dependence is close to 1 ($\approx$0.9). Approximation of this linear dependence to the value of the ZnSe energy gap gives for the I_D band maximum position a value $\sim$2.03–2.06 eV for the bulk ZnSe. This coincides with the

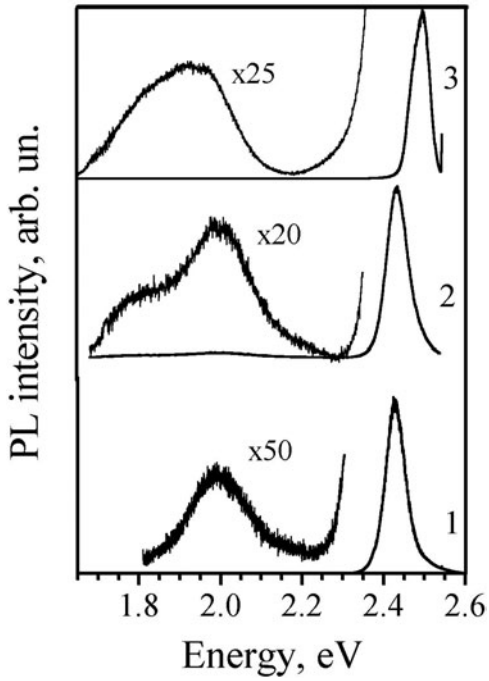

Figure 3. PL spectra of CdSe/ZnSe heterostructures with 12 vertically stacked CdSe layers of nominal thickness 3.5 ML at different temperatures and excitation wavelengths: $T = 300$ K, $\lambda_{exc} = 457.9$ nm (curve 1); $T = 300$ K, $\lambda_{exc} = 488.0$ nm (curve 2); $T = 77$ K, $\lambda_{exc} = 488.0$ nm (curve 3).

position of the self-activated emission in ZnSe caused by the radiative transition of an electron from the bottom of the conduction band to an acceptor level of the donor–acceptor pair D–V_{Zn} (so called A-centres) [5]. Such a band was observed in the PL spectra of the ZnSe epilayers studied (figure 1, curve 1). Therefore, it can be concluded that for all samples investigated the I_D band is connected with the A-centres. An additional proof of this nature of the I_D band is the dependence of its intensity on the VI/II group beam pressure ratio. In fact, a decrease of the VI/II beam pressure ratio from 5:1 (for multistack samples) down to 3:1 (in single-layer ones) that reduces the formation of V_{Zn} leads to the decrease of the I_D band intensity.

For single-layer structures the I_D band maximum position at $T = 77$ K depends weakly on the I_{QD} band one and lies in a higher-energy region in comparison with multistack samples containing CdSe inserts of the same nominal thickness (figure 1, curves 2, 4).

In the PL excitation spectra of the I_D band for multistack structures (figure 2, curve 3), besides the features corresponding to light absorption in the ZnSe barrier ($\sim$2.8 eV) and ZnCdSe wetting layer, two bands corresponding to e–hh and e–lh exciton transitions in QDs were found. For single-layer structures, only the features that corresponded to light absorption in the ZnSe barrier and ZnCdSe wetting layer were observed (not shown).

It was found that both the shape and the maximum position of the I_D band depend on the excitation light wavelength and temperature. In a number of cases the I_D band was the convolution of different bands. In figure 3 the PL spectra of multistack structures at different energies of excitation and temperatures are shown. It is seen that at 300 K under excitation in the ZnSe fundamental absorption region the I_D band is structureless and its maximum lies at $\sim$2.0 eV (figure 3, curve 1). Under excitation through the ZnCdSe wetting layer, besides a

maximum at ∼2.0 eV a shoulder at ∼1.85 eV appears (figure 3, curve 2). When the temperature is reducing, the total intensity of the I_D band increases. Since the intensity of the shoulder at ∼1.85 eV increases faster than the intensity of the maximum at ∼2.0 eV, the smoothing of the PL band shape and a shift of the total maximum position to the low-energy region are observed. It should be noted that for the single-layer samples the shift of the I_D band maximum while changing the energy of the excitation beam was insignificant (∼20 meV).

3. Discussion

The experimental results presented in the previous section give evidence that the centres responsible for the I_D emission at low temperature are localized on QDs at the interface. This conclusion is supported both by the I_D emission excitation spectra, where features typical of optical transitions in QDs are clearly pronounced, and by the quantitative correlation between the I_D and I_{QD} band maximum positions. The slope of the dependence of the I_D band maximum position on the I_{QD} one indicates that the radiative transition takes place from the quantized electron level of the QD to the acceptor level associated with the quantized heavy-hole level of the QD. This is in agreement with a cation vacancy-related nature of the defects investigated. In fact, in II–VI solid solutions the energy levels of cation vacancy-related defects are bound up with the valence band. A similar situation has been observed, for example, in CdS QDs embedded in glasses [6]. In the case of CdSe/ZnSe heterostructures a significant compressive strain in QDs should facilitate the vacancy-related defect accumulation at QDs.

As figure 3 shows, at room temperature the I_D band maximum position is close to 2.0 eV and corresponds therefore to the position of the self-activated emission in ZnSe. This means that A-centres are located in the ZnSe layers too. On the other hand, in the excitation spectra of the I_D band for single-layer samples only the peculiarities connected with light absorption in the ZnCdSe wetting layer and ZnSe layers were present. So we can state that the A-centres are also localized in the ZnCdSe wetting layer.

Thus, the I_D band consists of the emissions connected with the A-centres, which can be localized in different parts of the heterostructure: ZnSe layers, ZnCdSe wetting layers and on the QD interface.

The relative contribution of the emissions originating from different parts of the heterostructure to the I_D band should depend on the region where nonequilibrium carriers are generated (i.e. on the energy of excitation beam), its volume and optical density as well as on the velocities of nonequilibrium carrier capture and thermal escape for all regions. As was mentioned above, the I_D band maximum position for multistack structures at low temperatures depends weakly on the energy of excitation. This attests to a higher value of the capture velocity of nonequilibrium carriers generated in ZnSe or wetting layers by QDs. At room temperature, when thermal escape of carriers from QDs becomes crucial, emission bands connected with carrier recombination through the defects localized in wetting and ZnSe layers can appear in PL spectra (figure 3, curves 2, 3). Apparently, the shift of the I_D band to higher energies in single-layer structures in comparison with multistack ones is caused by the lower total volume of Cd-rich layers and by the higher contribution to the I_D band of the emission connected with the defects localized in ZnSe layers.

In conclusion, in the present work it is shown that defects including metal vacancies are localized, besides in the ZnSe barriers and the ZnCdSe wetting layers, also at the QD interface. The change of the temperature or energy of excitation allows separation of the contribution of the different parts of the heterostructure to the defect-related band. It is found that defect-related level in QDs is associated with the quantized heavy-hole level. Study of the excitation spectra of the defect-related band enables us to obtain information about optical transitions in QDs.

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