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Deep-level defects in CdSe/ZnSe QDs and giant anti-Stokes photoluminescence

M.Ya. Valakh, Yu.G. Sadofyev*, N.O. Korsunska, G.N. Semenova, V.V. Strelchuk, L.V. Borkovska, M.V. Vuychik, M. Sharibaev

Institute of Semiconductor Physics, NAS of Ukraine, 45 prospect Nauky, 03028 Kyiv, Ukraine
Phone: +38-044-2658550; fax: +38-044-2658342; e-mail: valakh@semicond.kiev.ua
**P.N. Lebedev Physical Institute, RAS, 117927 Moscow, Russia*

Abstract. CdSe/ZnSe structures with a quantum dot extrinsic photoluminescence band related to the defects that contain vacancies in cation sublattice has been investigated. It is shown that such defects can be localized in different parts of heterostructure (inside ZnSe barrier and cap layers, $Zn_{1-x}Cd_xSe$ wetting layer and at quantum dot heterointerface) and their localization depends on the preparation regimes and parameters of investigated structures. It is shown that defect level follows the heavy-hole related level. An intense anti-Stokes photoluminescence of quantum dots has been found. Two-step excitation mechanism of the anti-Stokes photoluminescence through the local states of investigated defects localized on the quantum dot interface is proposed.

Keywords: quantum dot, deep-level defects, anti-Stokes photoluminescence.

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1. Introduction

The CdSe/ZnSe-based quantum dot (QD) nanostructures are investigated widely because of the possible application for fabrication of blue-green lasers. In these systems a high concentration of cation vacancies is known to be generated during the growth processes. It can lead to the appearance of recombination channels that limit an efficiency of the QDs emission. On the other hand, lifetime of the carriers captured by such defects can be essentially higher and therefore these defects can be effective in the processes of anti-Stokes photoluminescence excitation [1]. In this work the influence of the defects including cation vacancies on the optical properties of heterostructures containing CdSe/ZnSe quantum dots has been studied. Anti-Stokes photoluminescence of quantum dots has been investigated.

2. Experiment and results

The studied structures were grown on GaAs(100) by MBE and contained either single sheet or twelve vertically stacked Cd-rich sheets separated by ~ 18 (or 50) nm ZnSe spacer. All samples were grown on 200 nm thick ZnSe buffer layer and were capped by 100 nm ZnSe layer. ZnSe buffer and ZnSe barriers were grown at the temperatures of 280 °C and 230 °C, correspondingly. 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. Time duration of both the temperature increase and decrease was 4 minutes. After such a procedure next ZnSe barrier or top layer was grown. The RHEED method was used to *in situ* control of three-dimensional island formation. Two series of multistack structures were grown. The samples of series 1 as well as single-sheet ones were grown at VI/II group beam pressure ratio of 3:1 while the samples of series 2 – at 5:1 ratio. In the samples of series 1 the nominal thickness of CdSe layer were 3.5 monolayer (ML) and ZnSe barrier thickness was 50 nm. In the samples of series 2 the nominal thickness of CdSe layers were 2.1–3.5 ML and the thickness of ZnSe barriers were 18 nm.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured in the temperature range 4.2–300 K. Photoluminescence was excited by the discrete lines of Ar^+ or N_2-laser. For PLE measurements a glow lamp was used.

The Fig.1 shows the PL spectra (curves 1) at $T = 77$ K of the single-sheet (*a*) and multistack (*b*, *c*) samples of series 1 (*b*) and 2 (*c*). In PL spectra of all the structures an intense band I_{QD} at 2.33–2.69 eV with FWHM of

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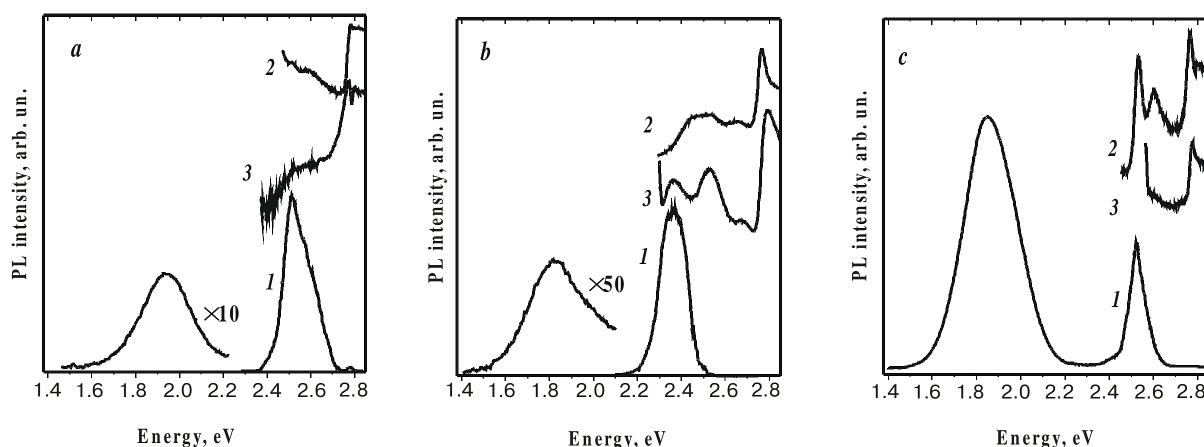

Fig. 1. PL (curve 1) and PL excitation spectra at T = 77 K of I_D (curve 2) and I_{QD} (curve 3) bands of structures contained single sheet Cd-rich dots (*a*) or twelve vertically stacked Cd-rich dots of series 1 (*b*) and 2 (*c*). The nominal thickness of CdSe layers is 3.5 ML, ZnSe barrier thickness is 50 nm (*b*) and 18 nm (*c*). λ_{exc} = 440 nm (curve 1).

28–115 meV and broad defect-related band I_D at 1.82–1.99 eV are observed. Increase of the nominal thickness of CdSe layer in multistack samples of series 2 results in the shift of both I_{QD} and I_D band maximum positions to the low-energy side of the spectral range (Fig.1, *c*). Spectral position of I_{QD} band is in agreement with the results obtained for the structures grown by the similar methods [2] where such band was interpreted as radiative recombination of the e-hh exciton in quantum dots.

The excitation spectra of I_D (curve 2) and I_{QD} bands (curves 3) are also presented in Fig.1. In PL excitation spectra of I_{QD} band (Fig.1, curve 3), besides the features corresponding to the light absorption in ZnSe-barrier (~ 2.8 eV), one can see the double band corresponding to heavy-hole and light-hole transitions in QDs. All these features are present in PL excitation spectra of I_D band (Fig.1, curve 2) of multistack samples of series 2 (Fig.1*c*) and single-sheet ones (Fig.1*a*). However, for single-sheet structures, the features corresponding to light absorption in QDs are not pronounced so clear. In PL excitation spectra of I_D band of the series 1 structures (Fig.1*b*, curve 2) only the features corresponding to light absorption in ZnSe barrier and $Zn_{1-x}Cd_xSe$ wetting layer (a shoulder in 2.4–2.7 eV range) are observed. It has been found that intensity, shape and spectral position of the maximum of I_D band depend essentially on the preparation regimes and parameters of investigated structures (number and nominal thicknesses of CdSe layers). In particular, in multistack samples an intensity of I_D band in the samples of series 2 is one order greater than intensity of such band in the samples of series 1. In multistack samples of series 1 (Fig.1*b*) the I_D band consists of two components, the spectral position of its high-energy shoulder is close to the spectral positions of the emission bands connected with the V_{Zn}-D defects observed in ZnSe layers [3].

Spectral position of I_D band has been found to depend on the energy of excitation quanta. The I_D band maximum position shifts to low-energy region under changing the excitation energy from 2.8 eV to 2.3–2.7 eV region. Nevertheless, for multistack structures this shift is small (~ 10 meV).

It should be noted that for all investigated samples a relation between I_D and I_{QD} band maximum positions is observed. However, a clear correlation is found only for the samples of series 2, for which the dependence of I_D band maximum position ($h\nu_D$) on the I_{QD} band maximum position ($h\nu_{QD}$) is linear (see Fig. 2, solid circles). The point corresponding to the structures of series 1 does not deviate from this dependence, if the low-energy edge of I_D band excitation spectra corresponding to the light absorption in wetting layer is taken instead of I_{QD} band maximum position. The point corresponding to the single-sheet sample is also presented in Fig.2 (open circle).

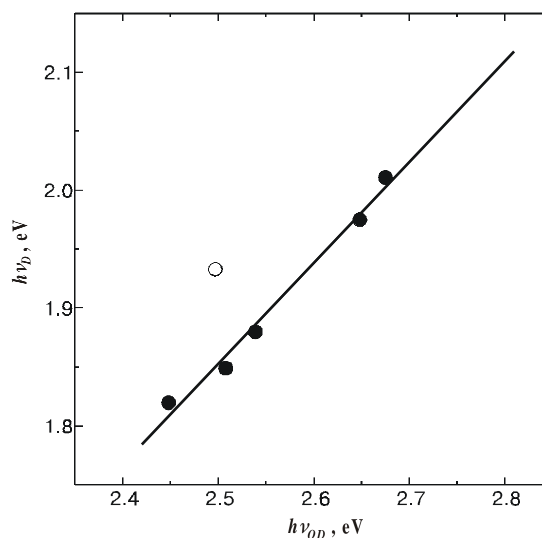

Fig. 2. Dependence of I_D band maximum position ($h\nu_D$) on the I_{QD} band maximum position ($h\nu_{QD}$) for multistack samples (solid circles) and single-sheet structure (open circle) at T = 77 K, λ_{exc} = 337 nm.

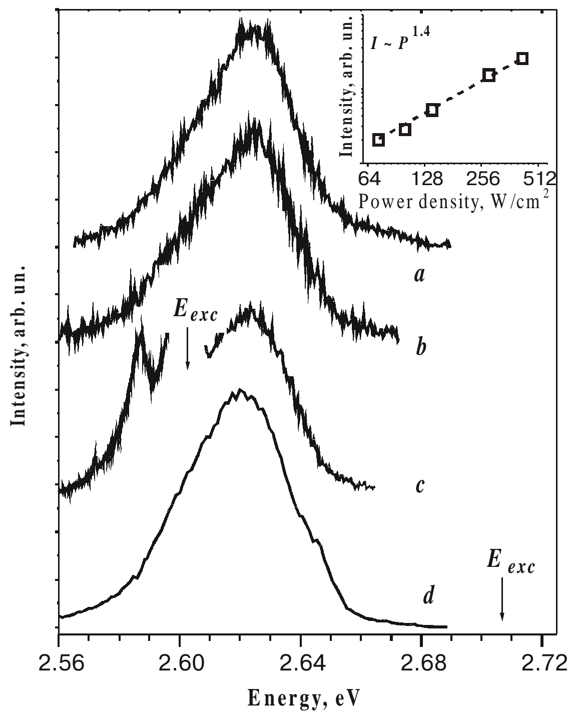

Fig. 3. Evolution of QD PL spectra at different values of excitation energy: *a* – 2.707; *b* – 2,602; *c* – 2.54; *d* – 2.41 eV.

The Fig. 3 shows the PL spectra of the sample of series 2 measured at T = 5 K under excitation on high-energy (E_{exc} = 2.71 eV) and low-energy (E_{exc} = 2.54 and 2.41 eV) sides of I_{QD} band as well as under resonant excitation (E_{exc} = 2.6 eV). It is seen that anti-Stokes PL band is somewhat shifted to high-energy region in comparison with Stokes band and has a smaller (by 3 to 5 meV) value of FWHM. The dependence of anti-Stokes PL on the excitation density was superlinear with the factor 1.4 (insert in Fig. 3). For the Stokes PL this dependence was linear. An efficiency of anti-Stokes PL was a few percents of the Stokes PL one. Under resonant excitation in QD PL band, the new band at 2.586 eV and with FWHM of 5 meV appears in the Stokes region. This band can be defined as an exciton recombination of the resonantly excited ensemble of QDs with the definite size and composition.

3. Discussion

Since the increase of Se flux pressure results in the increase of I_D band intensity, it can be concluded that this emission is connected with a cation vacancy related defect. Our results have shown also that I_D band consists of several PL bands connected with the defects localized in different parts of the heterostructure. Really, on the one hand, in the PL excitation spectra of I_D band the characteristic features corresponding to the light absorption in different parts of the structure (ZnSe barriers, wetting layer and quantum dots) are present. On the other hand, the I_D band maximum position depends on the region of heterostructure where carriers are generated. Moreover, in some samples the components of I_D band are resolved. For example, in multistack structures of series 1 (Fig.1*b*), two components are seen in the I_D band: the maximum and well resolved high-energy shoulder. It is naturally to relate the high-energy component with the centers localized in ZnSe barrier and the low-energy one – with the centers localized in the wetting layer. It is proved by the fact that only ZnSe barriers and wetting layer are observed in the excitation spectra of the I_D band. It should be noted that absence of the emission centers on the quantum dot interface in the samples of series 1 can be caused by larger sizes of these dots. Appearance of extended defects that are the sink for point defects is expected near such dots [3]. The bigger size of these dots in comparison with samples of series 2 that have the same 3.5 ML CdSe inserts is confirmed by more low-energy position of its I_{QD} band.

At the same time, in the samples of series 2, a considerable amount of defects is present on the quantum dot heterointerface (excitation through the quantum dots is effective). Observed insignificant difference in the I_D band maximum positions under excitation through the ZnSe barrier or QDs testifies to the main contribution into the emission of the defects localized at QD interface. Correlation of the I_D and I_{QD} band maximum positions means that the position of defect level on the quantum dot interface follows the quantized heavy-hole level of QDs. For the centers localized in the wetting layer (samples of series 1), the defect level follows the quantized heavy-hole level of the wetting layer. Approximation of the linear dependence presented in Fig. 2 to the bulk ZnSe gives the I_D band maximum position ~2.1 eV. Such emission band was really observed by us in ZnSe buffer layers [3]. The observed deviation of I_D band maximum position for single QD sheet samples from the linear dependence presented in Fig. 2 can be caused by the significant contribution of the emission from the defects localized in ZnSe because of relatively smaller amounts of CdSe in such structures.

The presence of significant quantity of cation vacancy related defects in investigated samples could cause observed intense anti-Stokes PL. In our case, the excitation mechanism of giant anti-Stokes PL can be in the best way explained by the two-step excitation process through the local levels of defects localized in Cd-rich layers. Really: i) in investigated samples these defects are present at QD heterointerface; ii) energy levels of such defects are enough deep. It is known that electron lifetime on the centers involving cation vacancy is sufficiently high (~10^{-3} c) [4]; iii) in the case of two-step excitation mechanism of the anti-Stokes PL, the intensity dependence on the excitation density could be characterized by the power law with the factor 2 and less, that is in agreement with experimental data obtained.

In conclusion, it should be noted that smaller value of FWHM as well as the shift of the anti-Stokes PL band maximum position in the high-energy region in comparison with the Stokes band can be explained in assumption

that the quantity of emission centers localized at QD interface decreases with increasing QD size. This is in agreement with earlier suggestion about the reasons of lack of such centers at QD interface in the samples of series 1.

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