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Study of thermal stability of CdSe/ZnSe quantum dot heterostructures

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Here we report on the effect of post-growth thermal annealing at 200-440 ºC on the photoluminescence (PL) characteristics of CdSe/ZnSe quantum dot (QD) and CdZnSe/ZnSe quantum well (QW) heterostructures grown by molecular beam epitaxy. After heat treatment at temperatures lower than 270 ºC, the PL intensity from both type of structures increases, while at temperatures above 270-340 ºC it decreases. A blue shift of the excitonic band position caused by Cd out-diffusion from the QDs (QWs) is observed above 320-340 ºC and is five times larger for the QD-related PL band than for the QW one. It is found that the energy of the excitonic transitions in the wetting layers does not change upon annealing. Lower thermal stability of the QDs as compared to that of the wetting layer and of the QW is explained by lateral Cd/Zn interdiffusion in the wetting layers via column II vacancies.

1 Introduction In the recent decade, the processes of quantum dot (QD) formation in CdSe/ZnSe heterostructures as well as their structural, optical and luminescent properties have been extensively studied [1-3]. An interest to CdSe QD heterostructures was stimulated not only by fundamental scientific reasons, but also by their potential application in light-emitting diodes and high power lasers operating in the green spectral region (500-550 nm) [4-6]. The devices utilizing CdSe QDs active region demonstrated a reduced threshold for optical pumping and higher degradation stability [4, 6] as compared to that based on the quantum wells (QWs). These advantages were explained by lower compressive strain in the QD active region [4] as well as by effective localization of carriers in the QDs that hinders their diffusion to the regions where carriers can recombine nonradiatively [6]. However, the degradation processes in CdSe QD heterostructures have not been studied in details.

Specifically, the degradation of the QW and QD lasers and laser structures is known to be accompanied by the shift of lasing spectra towards shorter wavelengths (blue shift) due to Cd/Zn interdiffusion across the heterointerfaces [7, 8]. The Cd/Zn interdiffusion stimulated by thermal annealing has been extensively studied in the QW structures [9, 10]. These studies have shown that diffusion of Cd from the QW is governed by column II vacancies (V_{Zn} or V_{Cd}). An intermixing of the materials of QW and the barriers upon thermal treatment has been found to occur via the vacancies generated at the surface of the sample and diffused into the structure [9]. In CdSe/ZnSe QD structures, the vacancy-related mechanism of Cd diffusion can also be supposed, but specific features of Cd/Zn interdiffusion can be expected due to the presence of Cd gradients inside the QD layer.

In this paper we report on a photoluminescence (PL) study of degradation of CdSe/ZnSe QD heterostructure upon the post-growth thermal annealing and compare it with that of CdZnSe/ZnSe QWs. For device application, the stacking of the QD layers is seems to be more attractive, as it allows a multiple increasing of the total number of QDs. Therefore, thermal stability of the multi stack QD structure emitted in the green was investigated here.

2 Experimental details The samples studied were grown on (001) GaAs substrate by molecular beam epitaxy. The QD sample consisted of a 250-nm thick ZnSe bottom layer, 12 vertically stacked CdSe sheets separated by ZnSe spacers of about 18 nm thickness and 150-nm thick ZnSe cap layer. The nominal thickness of each CdSe sheet was larger than 3.5 monolayers that exceeds the critical thickness of CdSe on ZnSe of about 3 ML and allows 3D-island formation. The QW sample contained a 700-nm thick ZnSe bottom layer and a CdZnSe/ZnSe multi QW structure covered by a 150-nm thick ZnSe cap layer. The QW structure composes of 30 $Cd_{0.45}Zn_{0.55}Se$ QWs each of about 5.5 nm thickness separated by 8 nm thick ZnSe layers. The composition and the thickness of the layers were determined *in situ* by the reflection high energy electron diffraction (RHEED) and specified by the simulations of the high-resolution X-ray diffraction (HRXRD) profiles.

The growth temperature was 280 ºC for ZnSe bottom layer and 230-250 °C for other layers. To stimulate the process of the QD formation 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 increase and the decrease in temperature was 4 min. The transition from 2D- to 3D-growth mode was *in situ* controlled by the RHEED. The method used here for QD formation is known to be suitable to achieve a stacking of several QD sheets with high optical quality and uniformity.

The HRXRD measurements were carried out using an X-ray diffractometer Philips MRD with a 4xGe (220) monochromator and Cu anode. The photoluminescence (PL) and PL excitation (PLE) measurements were done at 77 K. The PL spectra were excited by the emission of 250-W halogen lamp dispersed by a grating spectrometer and by a 365-nm line of 500-W Hg-lamp. The samples cut from wafer were thermally treated for 15 min at fixed temperatures from the range of 200-440 °C in nitrogen ambient to avoid surface oxidation.

3 Experimental results and discussion Experimental HRXRD ω/2θ (004) profiles of the initial QD and QW structures as well as corresponding simulations based on semikinematical diffraction theory are shown in Fig. 1.

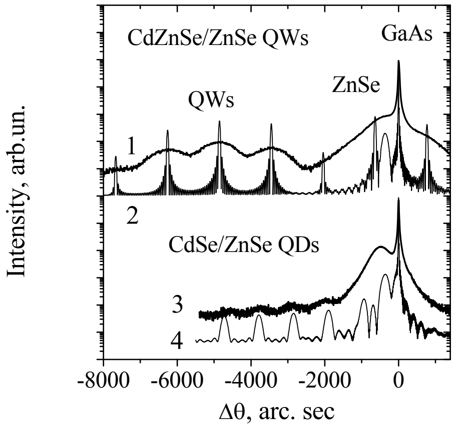

Figure 1 Experimental (1, 3) and simulated (2, 4) (004) HRXRD profiles for the initial QW (1, 2) and QD structures (3, 4).

On the low angle side from the substrate peak the signal from ZnSe layers modulated by interference is clearly observed. The interference is caused by the phase shift induced by the QD (QW) layers. In the QW sample, the signal from $Cd_{0.45}Zn_{0.55}Se$ QWs is also found. The parameters of the QW structure obtained from the simulations are presented in the previous section. In the QD sample, the simulations reveal the widening of $Cd_xZn_{1-x}Se$ QD layers up to 2 nm and their depletion with Cd down to x=0.7.

The PL and PLE spectra in the initial structures are shown in Fig. 2. The PL spectra of the structures consist of two bands: an intense band I_{QD} (I_{QW}) in the green region caused by radiative recombination of excitons in the QDs (QWs) and a broad band I_D in the red region caused by defect complex including column II vacancy [11, 12].

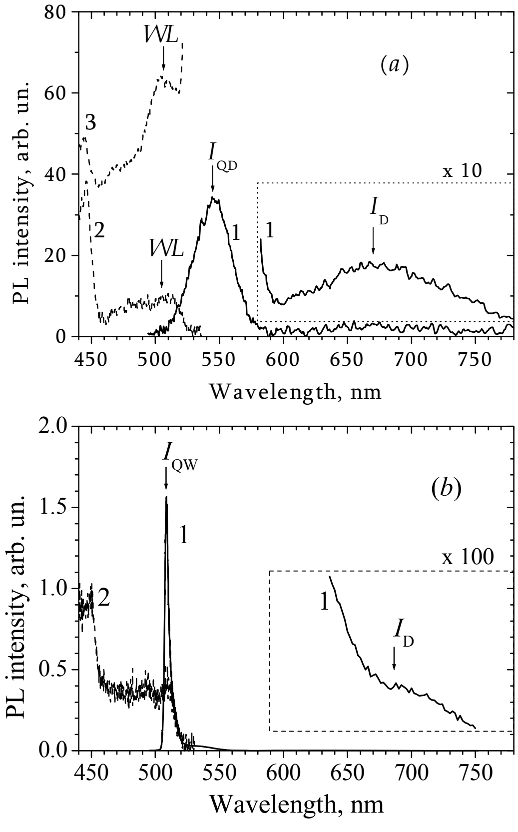

Figure 2 The PL (1) and PLE spectra of the I_D band (2) and I_{QD} band (3) in the initial QD (a) and QW structures (b). The PLE spectra are detected in low energy tail of the I_{QD} band and in the I_D band maximum. For the PL spectra λ_{exc}=440 nm; T=77 K.

In the PLE spectra of both the I_{QD} and I_D bands (Fig. 2a), the regions caused by absorption of excitation light in the ZnSe layers ($\lambda_{exc} \leq 445$ nm) and by continuous states of the wetting layers ($\lambda_{exc} < 510$ nm) can be defined. The peak *WL* observed on the long wavelength edge of the PLE spectra (Fig. 2a) can be ascribed to ground state heavy-hole-like exciton absorption in the wetting layers [11, 12]. The PLE spectrum of the I_D band in the QW structure (Fig.

2b) is determined by absorption of the excitation light in the ZnSe and QW layers, respectively.

Our previous investigations of the PL and PLE spectra in similar QD structures have shown that the column II vacancies are localized in both the ZnSe and the wetting layers of the structure [11, 12]. Therefore, the I_D band excited by light from ZnSe band-to-band absorption region consists of two bands: the first one caused by the defects located in ZnSe layers and the second one connected with the defects located in CdZnSe wetting (QW) layers. Since the spectral positions of these bands differ [12], the net position of the I_D band maximum depends on relative contribution of the two bands in the PL spectrum. In the initial samples, the I_D band maximum is close to that caused by the defects in the wetting (QW) layers.

Figure 3 shows the dependencies of the spectral position (a) and the intensity (b) of the PL bands and *WL* band in the PLE spectra on the annealing temperature T_{ann}.

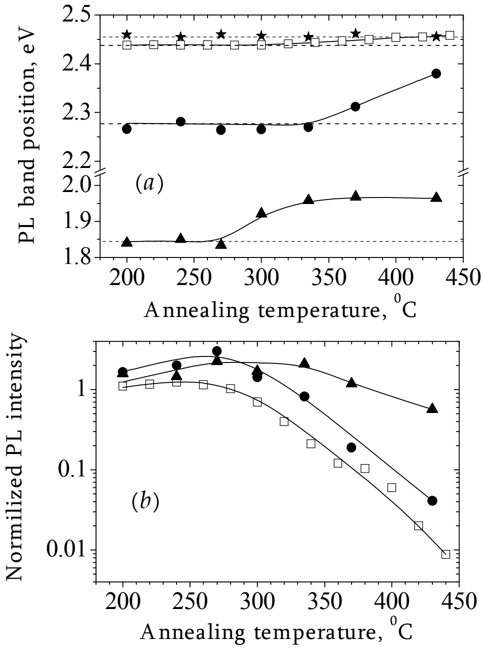

Figure 3 Spectral position (a) and PL intensity normalized to that in the initial samples (b) of the I_{QW} band (open squares) in the QW sample and I_{QD} (circles), I_D (triangles) and *WL* (stars) bands in the QD sample versus annealing temperature. Solid lines are drawn for better eye guide. Dashed lines (a) show spectral position of the I_{QD} and *WL* bands in the initial sample. λ_{exc}=440 nm, T=77 K.

At low annealing temperatures ($T_{ann} \leq 270$ °C), a spectral position of the PL bands does not change, while their intensity increases. The effect of PL intensity increase upon thermal annealing has been observed in CdZnSe/ZnSe QW heterostructures [13], as well as in InGaAs/GaAs QD heterostructures [14, 15] and ascribed to QW interface smoothing or nonradiative defect annealing. Since the intensities of the I_{QD} and I_D bands increase similarly, we suppose that it is due to annealing of the as-grown defects that act as the centers of nonradiative recombination.

At higher temperatures ($T_{ann} > 270$ °C), the PL intensity of both the QD- and QW-related excitonic bands falls down. The intensity of the I_D band decreases too, but more weakly. When the annealing temperature exceeds 320-350 °C, the QW- and QD-related bands start shifting to shorter wavelengths. A blue shift of the QD-related band upon annealing at 430 °C is five times larger that of the QW-related band indicating stronger degradation of the QDs as compared with the QWs. At the same time the spectral position of the *WL* band almost does not change in the whole range of the annealing temperatures.

The decrease in the PL intensity is caused mainly by generation of the centers of nonradiative recombination. Specifically, it can be due to multiplication of dislocations nearby the stacking faults at ZnSe bottom layer/GaAs substrate interface and their following growing into QD or QW layers. This has been proposed to explain a quenching of CdZnSe QW emission upon thermal annealing [16] as well as a rapid degradation of blue-green laser diodes based on CdZnSe QWs [7]. Another reason of PL intensity decrease can be the formation of the centers of nonradiative recombination or degradation of optical characteristics due to damage of the sample surface upon annealing. However, these can not explain smaller decrease in the intensity of the I_D band. Therefore, the increase in concentration of the defects giving rise to the I_D band and/or the decrease of recombination flow via QDs must be supposed.

The former can be due to generation of column II vacancies at the surface of the sample and their diffusion into the structure, as has been proposed for ZnCdSe/ZnSe QW heterostructures [9]. In the structures studied, this effect should result in the increase of contribution to the defect-related PL spectrum of the PL band connected with vacancy-related defects localized in the ZnSe layers. In fact, in the same range of the annealing temperatures (T_{ann}=300-335 °C), a blue shift of the I_D band towards that caused by the defects located in ZnSe layers, the broadening of I_D band and the decrease in relative contribution of *WL* peak in the I_D band excitation spectra were observed.

The decrease of recombination flow via QDs can be caused by Cd outdiffusion from the QDs, which results in the decrease of Cd content in the QDs and gradual dissolution of the QDs in the surrounding matrix. The outdiffusion of Cd from the QDs is proved by a noticeable blue shift of the QD emission band. The dissolution of the QDs would cause predominant decrease in the I_{QD} band intensity as well as the increase in the intensity of other recombination channels competing with the QD emission, in particular the I_D band intensity. Besides, in the PL spectrum of the QD structure annealed at 430 °C a new band appears in the short wavelength wing of the I_{QD} band at higher excitation power (Fig. 4, curve 2'). The spectral position of this band is close to the *WL* band position in the PLE spectra and can be ascribed to the emission from the wetting layers.

In contrast, no such band appears in the PL spectrum of the initial QD structure (Fig. 4, curve 1').

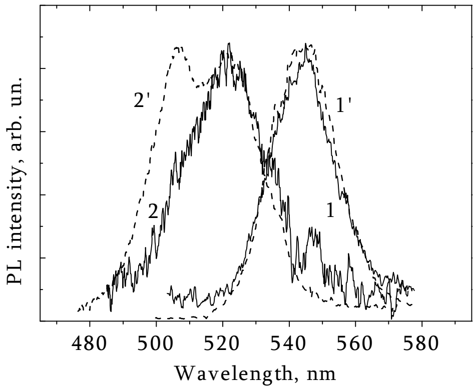

Figure 4 Normalized PL spectra in the initial (1, 1') and thermally annealed at 430 °C (2, 2') QD structures measured at the excitation power density of P_0 (1, 2) and 10 P_0 (1', 2'). T=77 K, λ_{exc}=365 nm.

The presented results implies that the column II vacancies diffused from the surface of the sample upon annealing, as well as the vacancies generated during the growth stimulate the process of Cd/Zn interdiffusion across the ZnSe/QD and ZnSe/QW interfaces which causes a blue shift of both the I_{QD} and I_{QW} bands. But in this case, not only Cd outdiffusion from the QDs but also Cd outdiffusion from the wetting layers to ZnSe should occur. However, we do not find an increase in the energy of excitonic transition in the wetting layers in contrast to that in the QWs and QDs (Fig. 3a). A similar effect, namely much larger blue shift of the QD emission band as compared to that of the wetting layer and QW emission bands, has been observed in some experiments on rapid thermal annealing of InAs/GaAs QD heterostructures [14, 15, 17, 18] and ascribed to the non-Fickian strain-enhanced lateral interdiffusion [17]. Structural investigations have proved that dissolution of InAs QDs in surrounding matrix occurs faster than that of the wetting or reference QW layers [15, 17] and that the lateral sizes of the QDs increase predominantly upon annealing [17] indicating lateral In/Ga interdiffusion. In our samples, the effect can be caused by strong lateral diffusion of Cd from the QDs in surrounding ZnCdSe wetting layer that hinders the blue shift of the *WL* band. We suppose that in contrast to the QW structures, the lateral Cd diffusion in the QD layer contributes noticeably to QD degradation and causes lower thermal stability of the QDs as compared to the QWs.

4 Conclusions Summarizing, we have found that the post-growth thermal annealing of Cd(Zn)Se/ZnSe QD and QW heterostructures influences the PL intensity and results in a blue shift of the QD and QW-related excitonic PL bands due to Cd/Zn interdiffusion. Although the intensities of the PL bands change similarly upon annealing, the blue shift magnitude is five times larger for the QDs than for the QWs. This means lower thermal stability of the QD structures as compared to the QWs, in spite of mentioned above higher degradation stability of QDs-based devices [4, 6]. It is proposed that lateral Cd/Zn interdiffusion in the QD layers via the column II vacancies contributes noticeably to QD degradation and causes its lower thermal stability.

References

[1] I. L. Krestnikov, N. N Ledentsov, A. Hoffmann, and D. Bimberg, Phys. Status Solidi A **83**, 207 (2001).

[2] E. Kurtz, J. Shen, M. Schmidt, M. Grun, S. K. Hong, D. Litvinov, D. Gerthsen, T. Oka, T. Yao, and C. Klingshirn, Thin Solid Films **367**, 68 (2000).

[3] T. Passow, K. Leonardi, H. Heinke, D. Hommel, D. Litvinov, A. Rosenauer, D. Gerthsen, J. Seufert, G. Bacher, and A. Forchel, J. Appl. Phys. **92**, 6546 (2002).

[4] A. Gust, C. Kruse, M. Klude, E. Roventa, R. Kroger, K. Sebald, H. Lohmeyer, B. Brendemuhl, J. Gutowski, and D. Hommel, Phys. Status Solidi C **2**, 1098 (2005).

[5] S. V. Gronin, S. V. Sorokin, I. V. Sedova, S. V. Ivanov, E. V. Zdanova, and M. M. Zverev, Phys. Status Solidi C **7**, 1694 (2010).

[6] S. V. Ivanov, A. A. Toropov, S. V. Sorokin, T. V. Shubina, A. V. Lebedev, I. V. Sedova, A. A. Sitnikova, R. V. Zolotareva, P. S. Kop'ev, and Zh. I. Alferov, J. Cryst. Growth **201/202**, 942 (1999).

[7] A. Ishibashi, J. Cryst. Growth **159**, 555 (1996).

[8] E. V. Lutsenko, A. L. Gurskii, N. V. Pavlovskii, V. Z. Zubialevich, G. P. Yablonskii, I. V. Sedova, S. V. Sorokin, A. A. Toropov, S. V. Ivanov, and P. S. Kop'ev, Phys. Status Solidi C **3**, 895 (2006).

[9] M. Kuttler, M. Strassburg, V. Turck, R. Heitz, U. W. Pohl, D. Bimberg, E. Kurtz, G. Landwehr, and D. Hommel, Appl. Phys. Lett. **69**, 2647 (1996).

[10] M. Kuttler, M. Strassburg, O. Stier, U. Pohl, D. Bimberg, E. Kurtz, J. Nurnberger, G. Landwehr, M. Behringer, and D. Hommel, Appl. Phys. Lett. **71**, 243 (1997).

[11] L. V. Borkovska, R. Beyer, M. Hoffmann, A. Holzhey, N. O. Korsunska, Yu. G. Sadofyev, and J. Weber, Defect Diffus. Forum **230-232**, 55 (2004).

[12] M. Ya. Valakh, Yu. G. Sadofyev, N. O. Korsunska, G. N. Semenova, V. V. Strelchuk, L. V. Borkovska, M. V. Vuychik, and M. Sharibaev, Semicond. Phys. Quantum Electron. Optoelectron. **5**, 254 (2002).

[13] M. Momose, A. Taike, M. Kawata, J. Gotoh, and S. Nakatsuka, Appl. Phys. Lett. **69**, 3572 (1996).

[14] S. Malik, Ch. Roberts, R. Murray, and M. Pate, Appl. Phys. Lett. **71**, 1987 (1997).

[15] S. J. Xu, X. C. Wang, S. J. Chua, C. H. Wang, W. J. Fan, J. Jiang, and X. G. Xie, Appl. Phys. Lett. **72**, 3335 (1998).

[16] G. Bacher, D. Tonnies, D. Eisert, A. Forchel, M. O. Mooler, M. Korn, B. Jobst, D. Hommel, G. Landwehr, J. Sollner, and M. Heuken, J. Appl. Phys. **79**, 4368 (1996).

[17] A. Babinski and J. Jasinski, Thin Solid Films **412**, 84 (2002).

[18] A. O. Kosogov, P. Werner, U. Gosele, N. N. Ledentsov, D. Bimberg, V. M. Ustinov, A. Yu. Egorov, A. E. Zhukov, P. S. Kop'ev, N. A. Bert, and Zh. I. Alferov, Appl. Phys. Lett. **69**, 3072 (1996).