ISSN: 2181-3906 2024

International scientific journal
«MODERN SCIENCE AND RESEARCH»
VOLUME 3 / ISSUE 2 / UIF:8.2 / MODERNSCIENCE.UZ

EFFECT OF TEMPERATURE ON THE OPTICAL PROPERTIES OF CDSE/ZNSE QUANTUM DOTS

Sharibaev M.B.
Xojaxmetova G.A.
Karakalpak state univessity named after Berdakh.
Saparniyazova G.
Karakalpak Institute of Agriculture and agricultural technologies, Nukus, Uzbekistan.

https://doi.org/10.5281/zenodo.10726640

Abstract. *The emission spectra of quantum-well CdSe/ZnSe heterostructures with quantum dots were determined by an optical method. CdSe/ZnSe heterostructures with quantum dots were grown at different temperatures; therefore, surface and deep-level minibands corresponding to the compositions of the structure were determined in the emission spectra. In the photoluminescence spectra, the shift of the radiative spectra is determined depending on the temperature of the grown quantum-size structures.*

Keywords: *Photoluminescence, photo reflections, quantum dot, relaxation.*

ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА ОПТИЧЕСКИЕ СВОЙСТВА КВАНТОВЫХ ТОЧЕК CDSE/ZNSE

Аннотация. *Спектры излучения квантоворазмерных гетероструктур CdSe/ZnSe с квантовыми точками определены оптическим методом. Гетероструктуры CdSe/ZnSe с квантовыми точками выращивались при разных температурах; поэтому в спектрах излучения определены поверхностные и глубокие мини-зоны, соответствующие составу структуры. В спектрах фотолюминесценции определяется сдвиг спектров излучения в зависимости от температуры выращиваемых квантоворазмерных структур.*

Ключевые слова: *Фотолюминесценция, фотоотражения, квантовая точка, релаксация.*

Introduction

In the recent decade, the processes of quantum dot (QD) formation in CdSe/ZnSe heterostructures grown by molecular beam epitaxy (MBE) as well as their structural, optical and luminescent properties have been extensively studied [1-4]. In particular, it was found that self-organization of CdSe QDs via Stranski-Krastanow growth mode is hindered by cadmium segregation [5, 6] and Cd/Zn interdiffusion [2, 7, 8]. It was shown that because of significant intermixing of CdSe and ZnSe layers a CdSe sheet transforms into cadmium enriched CdZnSe QDs of different sizes buried into 3-4 nm thick two-dimensional CdZnSe wetting layer [2, 4, 7]. The peculiarities of structural properties of epitaxial CdSe/ZnSe QD heterostructures determine their optical and luminescent characteristics in many respects [1, 3, 4].An interest to CdSe QDs grown by MBE was stimulated by their potential application in optoelectronic devices, in particular in green laser diodes instead of CdZnSe quantum wells (QWs). Green laser diodes based on II-VI compound low-dimensional structures are still of interest because of both absence of commercially available alternatives and high demands for such devices.

Specifically, they can be a new light source for plastic optical fibres with PMMA, compact full colour projector screens, laser TV projectors, etc. The first injection lasers and optically

pumped lasers that used the sheets with CdSe QDs as an active media demonstrated several advantages over QW-based devices, namely a reduced threshold for optical pumping and higher degradation stability. Heterostructures with CdSe QDs were found to be more stable against photo-degradation as compared to CdZnSe QWs. These advantages were explained by effective localization of carriers in QDs that hinders their diffusion to relaxed QDs and other regions where carriers can recombine nonradiatively and stimulate defect multiplication in the active region. However, degradation processes in CdSe QD heterostructures have not been studied in details. In particular, the peculiarities of Cd/Zn interdiffusion stimulated by external influences in asgrown CdSe QD heterostructures have not been studied at all. At the same time, it is known that degradation of light-emitting devices based on CdZnSe QWs is accompanied not only by noticeable reduction of QW emission caused by dislocation multiplication in active region, but also by the shift of QW emission band towards high energy spectral region (blue shift) due to Cd/Zn interdiffusion across QW heterointerface. Study of the processes of Cd/Zn interdiffusion in CdZnSe/Zn(S)Se QW heterostructures by applying thermal annealing revealed that diffusion of Cd from the QW is governed by column II vacancies (VZnor VCd) and the diffusion coefficient of Cd can be varied by about two orders of magnitude by varying the concentration of column II vacancies. [9-10]. It was shown also that intermixing of the materials of QW and the barriers under thermal annealing occurs via the vacancies generated at the surface of the sample and diffuse into the structure. In addition, we have found earlier in CdSe/ZnSe QD heterostructures that column II vacancies during the growth gather in the CdSe layers and influence significantly the QD selforganization process up to its full suppression. It can be supposed that presence of the vacancies in the wetting layer will influence degradation of QD luminescent characteristics, too.

In this paper, we report photoluminescence (PL) study of CdSe/ZnSe QD heterostructure subjected to thermal annealing with the aim to find a method for improvement of QD luminescent characteristics and to obtain additional information about their degradation connected with Cd/Zn interdiffusion.

Experimental details

The studied structure was grown on (001) GaAs substrate by MBE and contained 250-nm thick ZnSe buffer layer, 12 vertically stacked CdSe inserts separated by ZnSe spacers of about 15 nm thickness and 150-nm thick ZnSe cap layer. Nominal thickness of CdSe inserts was 5 monolayers. The growth rate was 5 nm/min. The growth temperature was 280 ºC for ZnSe buffer layer and 230 ºC for the rest of ZnSe layers as well as for CdSe layers. To stimulate QD formation, after the deposition of each CdSe layer the Cd beam was blocked, and the structure was heated up to 340 ºC and then cooled down to 230 ºC under Se flux. The duration of both steps was 4 min. The reflection high-energy electron diffraction(RHEED) was used for in situ control of threedimensional island formation.The PL signal was dispersed using a prism spectrometer (when the PL was excited by the light of a halogen lamp) or a grating spectrometer (when the PL was excited by the light of an Hg-lamp) and collected by photoelectronic multiplier.Samples cut from wafer were thermally treated for 15 min at 200, 220, 270, 300, 335, 370 and 430°C in nitrogen ambient to avoid surface oxidation.

Experimental results

ISSN: 2181-3906 2024

International scientific journal
«MODERN SCIENCE AND RESEARCH»
VOLUME 3 / ISSUE 2 / UIF:8.2 / MODERNSCIENCE.UZ

The PL spectrum of the as-grown sample is shown in Fig. 1a (curve 1). In the spectrum, the band I_{QD} peaking at 544 nm (2.277 eV) and caused by radiative recombination of excitons in QDs dominates. The full width at a half maximum (FWHM) of this band is ~100 meV and is related with dispersion of QDs both in composition and in size. In the PL spectrum, a defect related band I_D peaking at 670 nm (1.844 eV) and of ~300 meV FWHM is also present. The intensity ofID band is more than 10 times lower than that of I_{QD} band. Fig. 1a also shows the excitation spectra of both the QD and defect related bands (curves 2 and 3, correspondingly). The excitation spectrum of I_{QD} band was detected in the low energy tail of the band, while the excitation spectrum of I_D band was measured in the band maximum. In the spectra, in addition to the region caused by absorption of excitation light in ZnSe layers (λ=445 nm) two peaks can be distinguished: (i) the peak WL_{at} ~505 nm (2.455eV), and (ii) the peak X_{at} ~470 nm (2.638 eV). Our previous investigations of similar multistack QD structures have shown that the peak WL is caused by ground state heavy-hole-like exciton absorption in the wetting layer, while the peak X can be ascribed to ground state light-hole-like exciton absorption in the wetting layer. We have found earlier the linear dependence of the I_D band maximum position versus the spectral position of WL peak in I_D band excitation spectra. Approximation of this dependence to the value of the ZnSe energy gap revealed that I_D band is caused by defect complex including column II vacancy and shallow donor. Thus, the excitation spectra of I_D band indicate the presence of column II vacancies in the wetting layer of the as-grown sample. The changes introduced to the PL and PL excitation spectra by thermal treatment at 270, 300 and 370 °C are also depicted in Fig. 1b, c and d, correspondingly.

Fig. 1b shows that annealing at 270 °C results in a noticeable increase in the intensity of both the PL bands and in no change of their spectral position and excitation spectra. However, in the sample annealed at 300 °C the I_D band intensity stops growing, while the intensity of IQD band starts to decrease (Fig. 1c). These are accompanied by the shift to shorter wavelengths of the spectral position of the I_D band maximum and the decrease of WL peak intensity in its excitation spectrum. At the same time, no change is found in the excitation spectrum of the I_{QD} band.

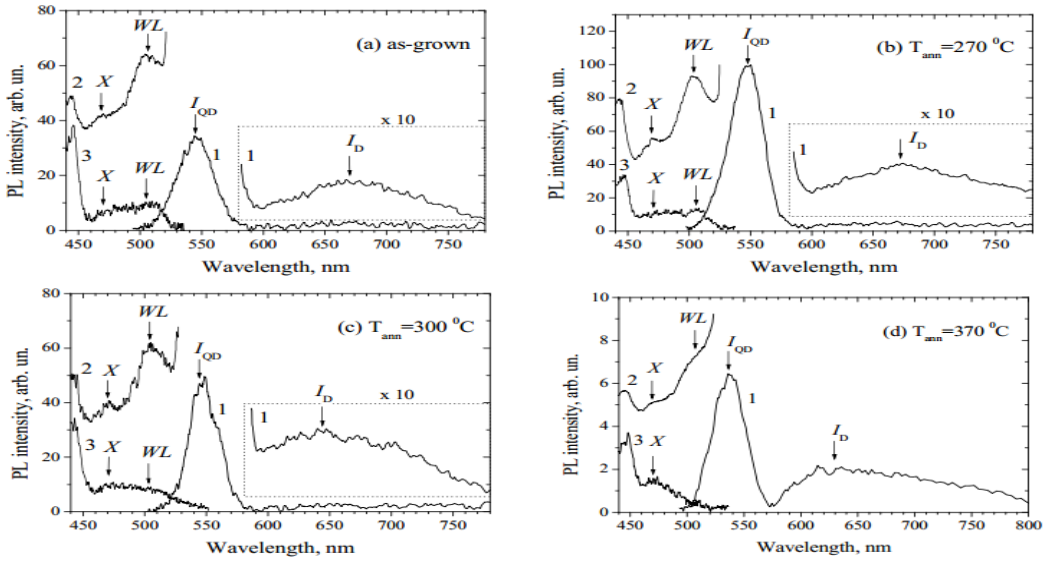

Fig. 1.PL (curves 1) and excitation spectra of I_{QD} band (curves 2) and of I_D band (curves 3) of the as-grown sample (a) and of the sample annealed at 270 (b), 300 (c) and 370^0C (d).

In the sample subjected to thermal annealing at 370 °C, the intensity of both PL bands decreases and their spectral position shifts to shorter wavelengths (blue shift) (Fig. 1d).

The excitation spectrum of I_{QD} band still does not change, but in the excitation spectrum of I_D band the intensity of WL peak keeps decreasing.

Thus, the post-growth thermal treatment of CdSe/ZnSe QD heterostructures results in changes in the PL intensity (at first the increase and then the decrease) and in the shift of PL band position to the high-energy spectral region (blue shift). The increase of the PL intensity is observed at low annealing temperatures (T_{ann}~270^0C) and is not accompanied by any change in the spectral position of PL bands or in their excitation spectra. The effect of PL intensity increase has been found earlier in CdZnSe/ZnSe QW heterostructures subjected to postgrowth thermal annealing at 250-700 0C and explained by interfacial smoothing resulting from the small-scale lateral diffusion.

The increase in the intensity of QW luminescence band was observed without any changes in its spectral position or with a noticeable blue shift. A similar effect was also found in the InGaAs/GaAs heterostructures with QWs or QDs subjected to thermal treatment and was ascribed to QW interface smoothing or nonradiative defect annealing. We suppose that the increase in intensities of both I_{QD} and I_D bands is the result of the annealing of as-grown defects (point defects, for example) that act as the centers of nonradiative recombination and are located in different layers of heterostructure.

The decrease in intensity of both PL bands observed at higher temperatures (Tann>270-3350C) is probably caused by generation of the centers of nonradiative recombination under thermal treatment. In particular, it can be due to multiplication of extended defects (dislocations) nearby the stacking faults at ZnSe buffer layer/GaAs substrate interface and their following growing into the active layers (QD layers). It was proposed earlier to explain both quenching of CdZnSe QW emission after rapid thermal annealing treatment and rapid degradation of blue-green laser diodes based on CdZnSe QWs.

However, the only rise of nonradiative defect concentration in the result of annealing can not explain different rates of the decrease of the I_{QD} and I_D band intensities. As it was mentioned above, quenching of the QD emission occurs much sharply than that of defectrelated band. This can be due to the increase of concentration of defects giving rise to I_D band and/or the decrease of QD concentration. Of the two mechanisms, the former can be realized if column II vacancies are generated during annealing at the surface of the sample and then diffuse into the structure as it was observed.

This explanation agrees with the blue shift of ID band position and the decrease of WL peak in its excitation spectra. Both of these are observed in the same range of annealing temperatures (T_{ann}=300-335^0C) and are very likely caused by the increase of contribution of emission of vacancy-related defects localized in the ZnSe layers to the I_D band (Fig. 1c, d). At the same time, the blue shift of defect-related band is accompanied by the increase of its FWHM, which in the sample annealed at 430^0C is 1.5 times larger than that in the as-grown one. In addition, the WLpeak decreases but not disappears in the ID band excitation

spectrum upon nnealing. These indicate that even after thermal treatment at 430 0C the I_D band emains mutlicomponent and the contribution of defects localized in the wetting ayers to the I_D band is large enough. The data obtained imply that the total concentration of column II vacancies increases in the structure.

Conclusions

In conclusion, we have found that post-growth thermal treatment of CdSe/ZnSe QD heterostructures influences the QD luminescence intensity and results in up to 100 meV blue shift of the QD luminescence band position. It is revealed that annealing of the samples at temperatures up to 270^0C allows raising the QD luminescence intensity by 2 to 3 times with no changes in other QD luminescent characteristics.

The effect is supposed to be due to annealing of as-grown centers of nonradiative recombination. The blue shift occurs at annealing temperatures of 370-430^0C concurrently with the decrease in the QD luminescence intensity and is not accompanied by the changes in the energy of the ground state excitonic transition in the wetting layer. This effect is ascribed to strain-enhanced lateral Cd/Zn interdiffusion in the QD layers through the vacancies generated during the growth of the structure.

REFERENCES

1. I.L. Krestnikov, N.N Ledentsov., A. Hoffmann and D. Bimberg, Arrays of two-dimensional islands formed by submonolayer insertions: growth, properties, devices // Phys. Stat. Sol. (a)83(2), p. 207-233 (2001).
2. N. Peranio, A. Rosenauer, D. Gerthsen, S.V Sorokin., I.V. Sedova and S.V. Ivanov, Structural and chemical analysis of CdSe/ZnSe nanostructures by transmission electron microscopy // Phys. Rev. B61(23), p. 16015-16024 (2000).
3. E. Kurtz, J. Shen, M. Schmidt, M. Grun, S.K. Hong, D. Litvinov, D. Gerthsen, T. Oka, T. Yao and C. Klingshirn, Formation and properties of self-organized II–VI quantum islands // Thin Sol. Films367, p. 68-74 (2000).
4. M. Strassburg, Th. Deniozou, A. Hoffmann, R. Heitz, U.W. Pohl, D. Bimberg, D. Litvinov, A. Rosenauer, D. Gerthsen, S. Schwedhelm, K. Lischka and D Schikora, Coexistence of planar and three-dimensional quantum dots in CdSe/ZnSe structures // Appl. Phys. Lett.76(6), p. 685-687. (2000).
5. T. Passow, K. Leonardi, H. Heinke, D. Hommel, D. Litvinov, A. Rosenauer, D. Gerthsen, J. Seufert, G. Bacher and A. Forchel, Quantum dot formation by segregation enhanced CdSe reorganization // J. Appl. Phys.92(11), p. 6546-6552 (2002).
6. H. Heinke, T. Passow, A. Stockmann, H. Selke, K. Leonardi and D. Hommel, Analysis of cadmium diffusion in ZnSe by X-ray diffraction and transmission electron microscopy // J. Cryst. Growth214/215, p. 585-589 (2000).
7. T. Passow, M. Klude, C. Kruse, K. Leonardi, R. Kroger, G. Alexe, K. Sebald, S. Ulrich, P. Michler, J. Gurowski, H. Heinke and D. Hommel, On the way to the II-VI quantum dot VCSEL // Adv. in Solid State Phys.42, p. 13-25 (2002).
8. 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, Ultra-low threshold

ZnSe-based lasers with novel design of ctive region // J. Cryst. Growth201/202, p. 942-945 (1999).

9. A. Ishibashi, II-VI blue-green light emitters // J.Cryst. Growth159, p. 555-565 (1996).
10. L.V. Borkovska, R. Beyer, M. Hoffmann, A. Holzhey, N.O. Korsunska, Yu.G. Sadofyev and J. Weber, Role of Cation Vacancy-Related Defects in Self-Assembling of CdSe Quantum Dots // Defect Diffus. Forum, 230-232, p.55-67 (2004).