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A new type of structural defects in CdZnSe/ZnSe heterostructures

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Abstract

The changes of structural and photoluminescence (PL) characteristics of MBE-grown CdZnSe/ZnSe single quantum well (QW) structures caused by Cd/Zn interdiffusion were studied by high-resolution X-ray diffraction (HRXRD) and low-temperature PL methods. The PL investigations showed that the increase of Cd content in the QW resulted in the increase of the depth of potential fluctuations in the QW as well as in the decrease of ZnSe cap layer band gap (up to several meV). The HRXRD scans as well as reciprocal space maps measured for symmetrical and asymmetrical diffractions revealed the formation of CdZnSe layers near the QW/ZnSe interface with Cd content of order of several percents. It is found that in some samples, the Cd profile in these layers is rather smooth while in others it is quite abrupt. In the latter case, the partial strain relaxation can occur in these layers.

Keywords: QW; ZnSe; CdSe; MBE; HRXRD; PL

1. Introduction

An interest to II–VI heterostructures that emerged more than a decade ago was caused by their potential application in opto-electronic devices operating in visible spectral range. Among them, CdSe/ZnSe nanostructures were the most widely investigated. However, up to now the lifetime of such devices remains a major problem [1].

Investigations of degradation processes in CdZnSe quantum wells (QWs) have shown that they are accompanied by electronically stimulated interdiffusion between barrier and well material [2]. To study Cd/Zn interdiffusion, a number of experiments dealing with ion implantation and thermal annealing of CdZnSe/Zn(S)Se QWs and short period superlattices were done [3–6]. It has been found that Cd diffusion is governed by column II vacancies mainly [3,5]. The extreme Cd diffusion enhancement in the case of p-type ZnSe doped by N [3] was attributed to generation of the compensating defect complexes including vacancies during the growth. These defects are supposed to migrate into the QW and cause degradation.

It should be noted that pronounced changes of the QW photoluminescence (PL) spectra caused by Cd/Zn interdiffusion were observed at annealing temperatures higher than 350–400 °C [4]. As a rule, Cd diffusion in ZnSe barriers is not taken into account at typical growth temperatures (~300 °C) especially if VI/II beam pressure ratio corresponds to stoichiometric growth conditions. However, early reflective high-energy electron diffraction (RHEED) and transmission electron microscopy measurements of CdSe/ZnSe QWs have shown that it is impossible to grow pure CdSe QWs between ZnSe barriers at temperatures above ~180 °C due to intermixing of the QW and barrier material [6]. This means that interdiffusion can also influence the growth processes of CdZnSe/ZnSe QW structures.

In this paper, we present the results of our investigations by low-temperature PL and high-resolution X-ray diffraction (HRXRD) of Cd/Zn interdiffusion, which occurs during the growth in the CdZnSe/ZnSe single QW structures.

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2. Experimental procedure

The structures under investigation were grown by molecular beam epitaxy (MBE) on n+-GaAs (1 0 0) substrates at VI/II group beam pressure ratio of 2:1. ZnSe barriers were grown at ~320 °C, while CdZnSe QW at ~280 °C. The growth rate was 300–500 nm/h. In situ RHEED was used to check the growth rate of ZnSe and QW layers.

All the structures were grown on 1300 nm thick ZnSe buffer layer and capped by 250 nm thick ZnSe layer. The QW thickness was ~6 nm and the molar fraction x of cadmium in $Cd_xZn_{1-x}Se$ QWs was 0.21, 0.23, 0.35 and 0.4 in different samples.

The HRXRD measurements were carried out using a high-resolution X-ray diffractometer "X'Pert PRO MRD XL" with a 4 × Ge(2 2 0) monochromator, a 3 × Ge(2 2 0) analyzer and a Cu anode. For all structures studied, reciprocal space maps (RSM) for symmetrical 004 and asymmetrical 113 and 224 diffraction geometries as well as individual scans were registered. The PL spectra were measured at 5 K under excitation by 325 nm line of He–Cd laser.

3. Experimental results and discussion

Fig. 1 presents 5 K PL spectra of the structures studied. These spectra are dominated by emission band caused by radiative recombination of excitons bound on defects or localised by potential fluctuations in the QW [7].

In the samples with lower Cd content (x~0.2), the QW PL band consists of two components (curves 1, 2 in Fig. 1). Spectral separation between these components is about 7 meV that is similar to the one observed for shallow donor-bound excitons in MBE-grown ZnSe layers [8]. Similar situation was found in [7] where the low-energy component was attributed to a donor-bound exciton emission in the QW while the high-energy one was ascribed to emission of excitons localised by potential fluctuations in the QW.

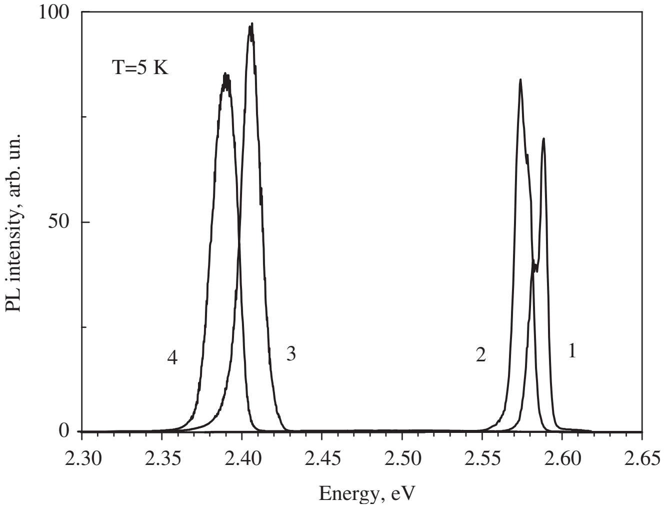

Fig. 1. The photoluminescence spectra of $Cd_xZn_{1-x}Se$/ZnSe single QWs with $x = 0.21$ (curve 1), 0.23 (curve 2), 0.35 (curve 3) and 0.4 (curve 4). $T = 5$ K, $\lambda_{exc} = 325$ nm.

The PL band of the QWs with higher Cd content (x~0.3–0.4) is a single component (curves 3, 4 in Fig. 1). The full-width at a half-maximum (FWHM) of this band is ~15–18 meV that is higher than the FWHM of the band in the QWs with x~0.2 (~10–11 meV). This band is obviously due to emission of excitons localised by potential fluctuations caused by local composition disorder in the QW.

The excitonic spectra of ZnSe layers in the structures studied are shown in Fig. 2 by curves 1–4. The PL spectrum of excitonic emission in 1300 nm thick ZnSe epilayer grown on GaAs substrate in the same conditions as a buffer layer is presented in Fig. 2 by curve 5.

The PL spectrum of ZnSe epilayer consists of free exciton band splitted by the deformation potential on heavy-hole X_{hh} and light-hole X_{lh} components, the peaks I_1 and I_2 caused by excitons bound to neutral acceptors and neutral donors, respectively [8], as well as I_V^0 line related to exciton recombination on threading dislocations [9]. The value of relative deformations ε in ZnSe layers can be

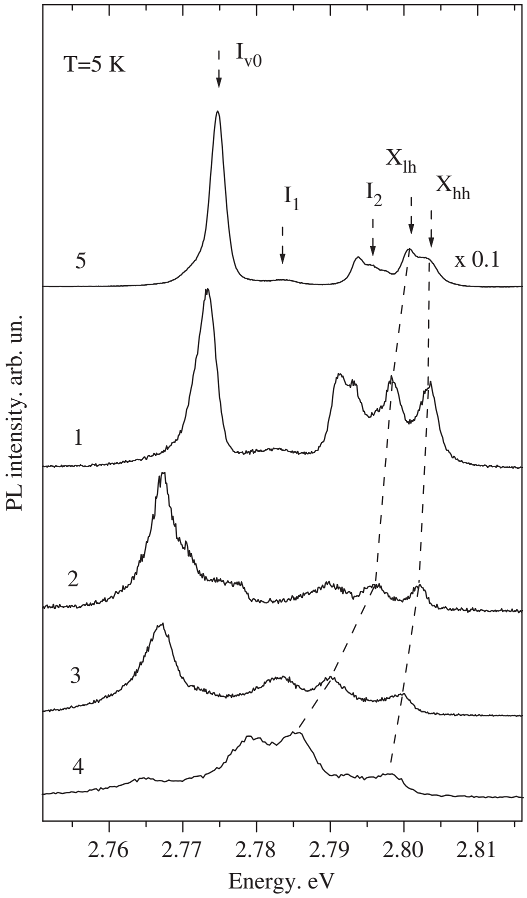

Fig. 2. Excitonic spectra of ZnSe cap layers in $Cd_xZn_{1-x}Se$/ZnSe single QW structures with $x = 0.21$ (curve 1), 0.23 (curve 2), 0.35 (curve 3) and 0.4 (curve 4). Edge emission of ZnSe epilayer of 1300 nm thickness (curve 5) is shown for comparison. $T = 5$ K, $\lambda_{exc} = 325$ nm.

estimated from the energy difference between X_{hh} and X_{lh} components that is expressed by

$$X_{\mathrm{hh}} - X_{\mathrm{lh}} = -2b\varepsilon\frac{C_{11}+2C_{12}}{C_{11}},$$

where $b = -1.2\,\mathrm{eV}$ is the shear deformation potential, $\mathrm{C}_{11} = 8.59\times10^{10}\,\mathrm{N/m^2}$ and $\mathrm{C}_{12} = 5.06\times10^{10}\,\mathrm{N/m^2}$ are the elastic stiffness constants for ZnSe [8].

The estimations show tensile relative deformations $\varepsilon = 0.66\times10^{-3}$ in ZnSe epilayer which are caused by different thermal expansion coefficients of ZnSe and GaAs.

As Fig. 2 shows, the increase of Cd content in the QWs results in the low-energy shift of all ZnSe excitonic lines and in the increase of the energy difference between X_{hh} and X_{lh} peaks. Following the evaluation procedure of relative deformations executed for ZnSe epilayer, we obtain the rise of tensile relative deformations in ZnSe layers with the increase of Cd content in the QW: $\varepsilon = 0.92\times10^{-3}$ $(x = 0.21)$, $\varepsilon = 1.1\times10^{-3}$ $(x = 0.23)$, $\varepsilon = 1.8\times10^{-3}$ $(x = 0.35)$ and $\varepsilon = 2.3\times10^{-3}$ $(x = 0.4)$. However, recalculation of the spectral position of X_{hh} and X_{lh} peaks to the point $\varepsilon = 0$ reveals that free exciton line position in ZnSe layers shifts systematically to the low-energy region with the increase of x (up to 3 meV in the sample with $x = 0.4$). This can be ascribed to the decrease of the layer band gap due to the formation of ZnCdSe solution with about several tenths of percent of Cd. Diffusion of Cd into ZnSe layers can also be the reason of the broadening of all excitonic lines and the decrease of I_{V}^{0} line intensity that is known to be very sensitive to the presence of impurities [9]. Hence, excitonic spectra of ZnSe layers are found to be more sensitive to interdiffusion processes than the QW band. Taking into account ZnSe band-to-band absorption coefficient ($\sim10^{5}\,\mathrm{cm^{-1}}$) and decrease of diffusion length of carriers in ZnSe due to effective capture and recombination of carriers in QWs, we can think that ZnSe excitonic emission is excited mainly in the cap layer. Thus, our PL investigations show that at least ZnSe cap layer suffer from Cd diffusion.

To obtain more information about interdiffusion in the structures studied, the (0 0 4) $\omega/2\Theta$ HRXRD scans were measured (Fig. 3). In all the curves presented in Fig. 3, the peak from ZnSe layers as well the intense peak from GaAs substrate are found. Relative angular spacing between these two peaks is close to one observed for almost fully relaxed ZnSe layers grown on GaAs substrate [10]. However, in some samples (Fig. 3, curves 2, 4), additional peaks appear on the low angle side of ZnSe peak. These peaks cannot be the interference fringes because of a thick ZnSe buffer, which contains high dislocation density near the ZnSe/GaAs interface. ZnSe regions that are located near the dislocation network and have different tilt angle and tilt direction with respect to the crystallographic directions in the plane of the substrate can cause in principle these additional maxima [10]. A doping of ZnSe layers by Cd can also result in the appearance of these peaks.

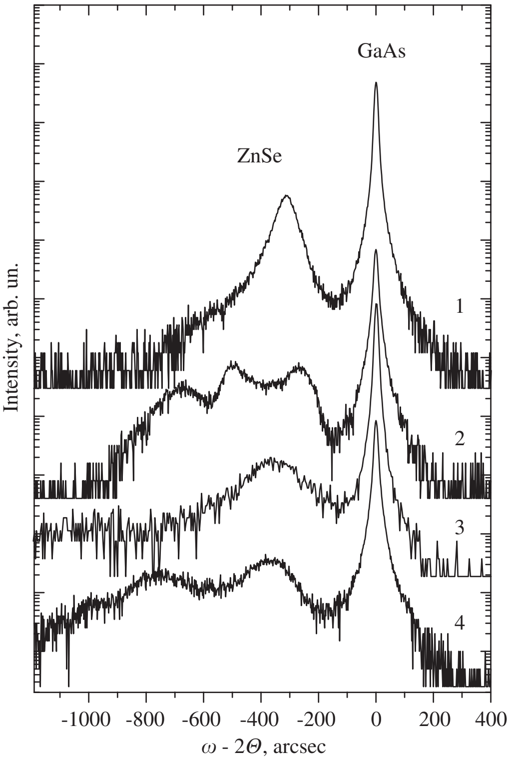

Fig. 3. Experimental HRXRD (0 0 4) $\omega/2\theta$-profiles of $\mathrm{Cd}_x\mathrm{Zn}_{1-x}\mathrm{Se/ZnSe}$ single QW structures with $x = 0.21$ (curve 1), 0.23 (curve 2), 0.35 (curve 3) and 0.4 (curve 4).

To make a choice between these two possibilities as well as to obtain a strain status of the structures studied, the RSM in the vicinity of the (0 0 4), (2 2 4) and (1 1 3) reciprocal lattice points (RLP) of the substrate were measured. The RSMs in the vicinity of the (0 0 4) RLP of the substrate measured by varying the azimuth angles (0°, 90° and 180°), show that additional maxima observed on the low angle side of ZnSe peak do not originate from ZnSe layers with different tilt angle. It was also found that the angle of inclination between ZnSe layers and GaAs substrate was 97° and 198° in the samples without additional maxima ($x = 0.21$ and 0.35, respectively) and $<40°$ in the structures with additional maxima ($x = 0.23$, 0.4).

Fig. 4(a)–(c) shows the measured RSM in the vicinity of the (1 1 3) RLP of the substrate for the QW structures with $x = 0.35$, 0.23 and 0.4, respectively. The maps present the isointensity contours of scattered X-ray radiation, where the Qx axis is parallel to the [1 1 0] direction and the Qy axis is parallel to the [0 0 1] growth direction.

The RSMs show that in the samples with $x = 0.21$ and 0.35, the QW grows pseudomorphically on ZnSe buffer. However, the RLP of ZnSe layer is found to stretch towards the RLP of QW. This can be ascribed to the formation of ZnCdSe layer with rather smooth Cd profile. It obviously becomes apparent as a shoulder at the low angle side of ZnSe peak in the (0 0 4) $\omega/2\Theta$ scans (Fig. 3, curves 1, 3).

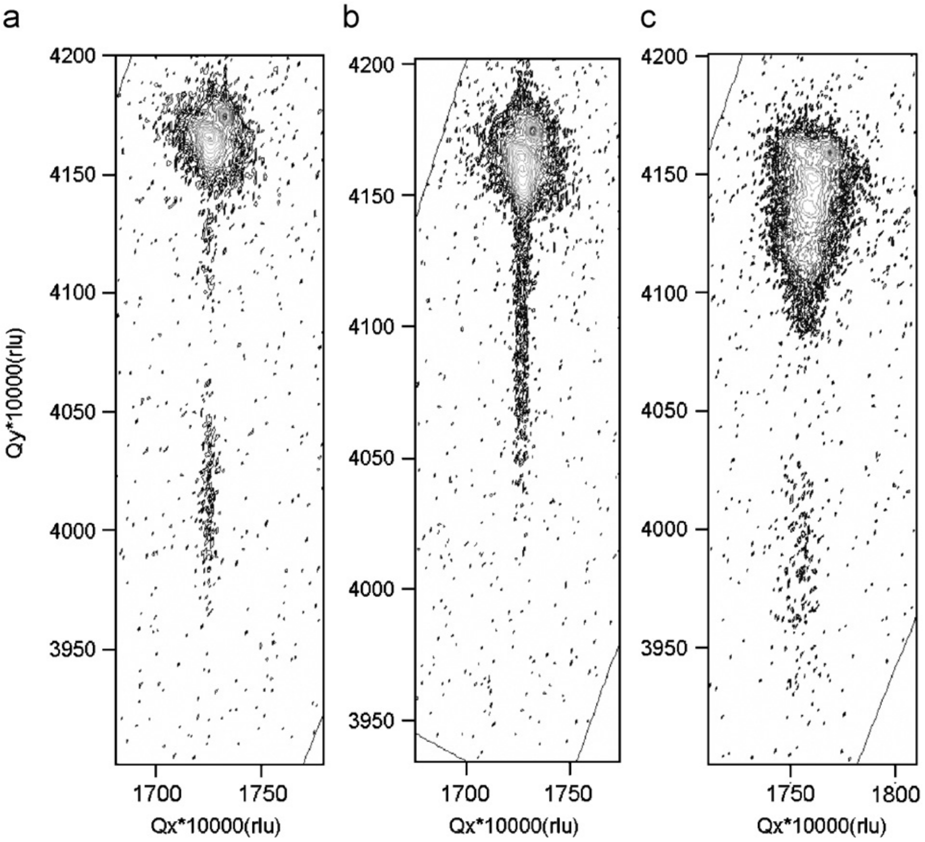

Fig. 4. Reciprocal space maps in the vicinity of the (1 1 3) reciprocal lattice points of the substrate for $Cd_xZn_{1-x}Se$/ZnSe single QW structures with $x = 0.35$ (a), 0.23 (b) and 0.4 (c).

In the samples with $x = 0.23$ and 0.4, the RSMs in the vicinity of ZnSe RLP are more complicated (Fig. 4b and c). The scattering intensities from Cd-doped ZnSe layers appear as two distinct intense peaks corresponding to two individual ZnCdSe layers with different Cd content. This means that in these structures the ZnCdSe layers have sharper interfaces than in the samples with $x = 0.21$ and 0.35. Simulations of (0 0 4) $\omega/2\Theta$ scans based on dynamical diffraction theory show that the increase of Cd content in the QW leads to the increase of Cd content in both of ZnCdSe layers amounting 10% and 5% in the QW structure with $x = 0.4$. In the sample with $x = 0.23$, the QW as well as ZnCdSe layers are grown pseudomorphically on ZnSe buffer (Fig. 4b). But in the sample with $x = 0.4$, both ZnCdSe layers are partially relaxed (Fig. 4c); the lower the Cd content in the layer, the stronger is the relaxation. In this case, QW is pseudomorphically strained with respect to ZnCdSe layer with higher Cd content.

Hence, the HRXRD investigations show that during the growth a significant Cd diffusion from QW in surrounding ZnSe layers occurs resulting in formation of ZnCdSe layers with Cd content of order of several percents. The PL spectra demonstrate that even near the surface region, the ZnSe cap is doped with Cd up to several tenths of percent.

Since the excitonic spectra of ZnSe cap layer do not change noticeably from sample to sample (Fig. 2) reflecting the change of strain and Cd doping level only, we can speculate that the growth procedure remains the same in all the samples. We suppose that different character of Cd distribution in ZnCdSe layers revealed by HRXRD originates from the change of the angle of inclination between ZnSe layers and GaAs substrate. This can result in changes of atom sticking coefficient during the growth process. In fact, the decrease of Cd content in CdZnSe/ZnSe QW as well as the decrease of the well thickness were observed under the growth on inclined substrates [11]. Study of strain relaxation in MBE-grown ZnSe/GaAs (0 0 1) heterostructures [10] has proved that a mean value of inclination angle remains pretty constant for the pseudomorphic layers, but some occasional change from sample to sample after the strain relaxation occurs. So, we suppose that occasional changes of inclination angle during the growth of thick ZnSe buffer result in the changes in the QW growth kinetics and interdiffusion processes.

4. Conclusion

The PL and structural properties of CdZnSe/ZnSe single QW structures were investigated by the PL and HRXRD methods. Analysis of the excitonic PL spectra of QW and ZnSe cap layers reveals that the increase of Cd content in the QW results in the increase of the depth of potential fluctuations in the QW caused by local compositional disorder as well as in the increase of planar tensile strains and enhancement of Cd diffusion in ZnSe layers. The HRXRD investigations proved significant Cd diffusion in ZnSe that can result in formation of ZnCdSe layers with abrupt interfaces and relatively high Cd content (up to 5% and 10% in the QW structure with $x = 0.4$). It is found that in some cases partial strain relaxation can occur in these layers. Occasional changes of inclination angle between thick ZnSe buffer layer and GaAs substrate that accompany strain relaxation during the growth are supposed to be the reason of observed differences in interdiffusion processes between the samples.

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