Investigation of depth inhomogeneity of ZnTe, CdZnTe, ZnSe epilayers grown on (001)GaAs by MBE

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ABSTRACT

In this work we report the depth inhomogeneity study of MBE grown ZnSe, CdZnTe and ZnTe/(001) GaAs epilayers of different thickness by X-ray and depth resolved photoluminescence methods. Step etching and different wavelength excitation were used for this purpose. It is shown that all these epilayers consist of three regions with different extended defect and impurity concentration: (i) near the interface one with high density of misfit dislocations and impurities concentration; (ii) the region with low extended defect and impurity concentration and (iii) near the top surface region with higher extended and point defect concentration. The deterioration of near top surface region increases with epilayer thickness. Influence of GaAs substrate preparation regimes on ZnSe layer growth and optical properties as well as the study of interdiffusion of Ga and Zn across the wafer-epilayer interface have been investigated. The possibility to use thin intermediate ZnTe layer with solid phase crystallization (surfactant) for blocking of the interdiffusion in ZnTe layers and improvement of epilayer photoluminescence characteristics have been explored.

Keywords: molecular beam epitaxy, photoluminescence, ZnSe/GaAs, ZnTe/GaAs, ZnCdTe/GaAs epilayers, depth inhomogeneity.

1. INTRODUCTION

High quality ZnSe, ZnTe and CdZnTe epitaxial layers, ELs, on GaAs substrates are of great interest as a components of different optical devices, including infrared ones: laser systems, photodetectors, solar cells, photorefractive devices, etc.[1-3]. GaAs crystals are widely used as a substrate for MBE growth of II-VI layers because of: (i) lack of high quality and large areas II-VI bulk single crystals[4]; (ii) high cost of bulk II-VI substrates, and (iii) as the treatment of III-V compounds is well known[5].

However, some problems connected with GaAs as a substrate exist: (i) lattice mismatch (~7.6% for ZnTe/GaAs and 0.27% for ZnSe/GaAs at room temperature) and thermal expansion differences which result in strain in these systems; (ii) interdiffusion of the components across the interface. These both factors can result in depth inhomogeneity of ELs and promote the degradation processes in optoelectronic devices based on these systems.

In this paper we present a study of depth inhomogeneity in ZnTe, CdZnTe and ZnSe epitaxial layers of different thickness grown by MBE on GaAs substrates. The influence of growth temperature, flux ratio and (001) GaAs substrate preparation on ZnSe layer growth and optical characteristics as well as Ga and Zn interdiffusion across the wafer/epilayer interface have been investigated. Besides the effect of thin intermediate ZnTe layer subjected to solid phase crystallization on extended defect distribution and interdiffusion process have been explored in ZnTe layers by optical and X-ray methods.

2. EXPERIMENTAL AND SAMPLES TREATMENT

All nominally undoped ZnSe, ZnTe and CdZnTe layers with different thickness (0.5-2.7 μm) were grown by MBE method on semiinsulating Cr-doped (001) GaAs substrates in a CATYN' machine equipped with conventional effusion cells for high purity elements. The residual pressure in the chamber was $\sim 8\cdot 10^{-11}$ Torr. For deoxidation the GaAs substrates were heated up to a temperature of about 580 °C without or with the use of an As beam. Reflection high-energy electron

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diffraction, RHEED, was applied to control the surface during deoxidation and deposition processes. It is essential that before the deposition of ZnSe epilayer GaAs surface was treated in Zn flux during 100s at pressure $\sim 4 \cdot 10^{-7}$ Torr for prevention the chemical reaction of Se and the excess Ga on the GaAs surface. In the case of intermediate ZnTe layer application the oxide-free GaAs substrate was cooled down to room temperature and covered by an amorphous 5 nm ZnTe layer which was then crystallized by heating up to growth temperature. The subsequent procedure was the growth of ZnTe thick (1.5-2 μm) buffer layer. The growth temperatures were 260-340°C for ZnSe, 350 °C for ZnTe, and 300 °C for $Cd_{0.4}Zn_{0.6}Te$ ELs and Zn/Te or Se/Zn beam pressure ratios were I_{Zn}/I_{Te}=1:2 and I_{Se}/I_{Zn}=1.2-1.5 for ZnTe and ZnSe, respectively. Typical growth rate was ~0,6 μm/hour. The free carrier concentration, n, and mobility, μ, were obtained from Hall effect measurements at 300 K.

We used X-ray diffraction and X-ray topography methods combined with exciton and impurity luminescence spectroscopy as well as light reflection measurements to control the epilayer properties. Photoluminescence, PL, of ZnSe and ZnTe was excited by the mercury 200 W lamp (λ_{exc}=365 nm) and Ar^+ laser (λ_{exc}=0.4765, 0.4880, 0.5145 nm), respectively. PL of GaAs was excited by a He-Ne laser (λ_{exc}=632.8 nm). PL spectra were recorded in the range from 440 nm (2.805 eV) to 1400 nm (0.885 eV) in temperature interval 4.2÷77 K and at 300 K using the grating spectrometer MDR-23 and in the range from 1000 to 2000 nm using prismatic spectrometer (IKS-type). For reflection spectra measurements a glow lamp was used. Depth inhomogeneity of ZnSe ELs have been investigated with step etching in special solution which contained Br_2, HCl and dioxane[6]. Depth distribution of radiative centers in ZnTe ELs have been studied by PL method using the excitation by the light of different wavelengths[7] that correspond to different absorption coefficients ($\alpha \approx 10^4 \div 10^5$ cm^{-1} for $\lambda \approx 0.476 \div 0.514$ nm).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 ZnSe epilayers

Three typical PL spectra measured at 4.2 K are shown on Fig.1. These spectra correspond to ZnSe epilayers which were grown under practically identical conditions and differed in their thickness, t, only (curves a, b, c). The spectra of thick samples (t>1 μm) (curve b, c) in the band-edge energy and donor-acceptor pair, DAP, recombination regions consist of narrow bands with peak position at $h\nu_{m1}$=2.802 eV (442 nm), $h\nu_{m2}$=2.796 eV (443.5 nm), $h\nu_{m3}$=2.772 eV (446.8 nm) and $h\nu_{m4}$=2.602 eV (476.5 nm). The position of first PL emission band corresponds to free exciton transition and labeled as I_{FX}. On more large scale it consists of two peaks (main peak and shoulder at higher energy). This double peak can be

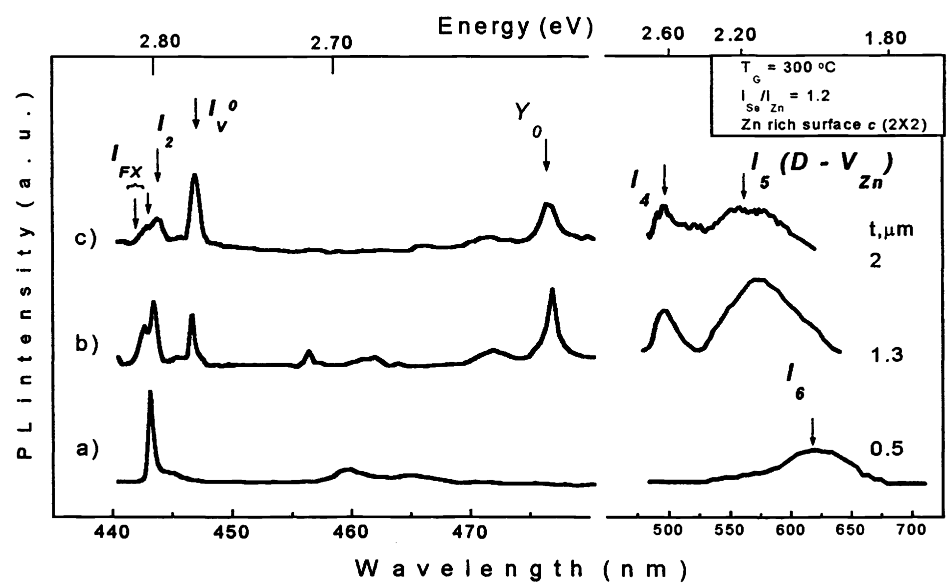

Fig.1. Typical 4.2 K photoluminescence spectra of a nominally undoped ZnSe films with different thickness, t, deposited directly on (001) GaAs substrates at identical growth parameters, which are given in the insert.

ascribed to valence band split on light-hole, lh, and heavy-hole, hh, branches due to the strain[8]. The position of the main peak (lh branch) is more sensitive to the strain and shifts to lower energy for thicker layers. It apparently is connected with the increase of tensile strain with the increase of ZnSe/GaAs ELs thickness. The position of second PL band (443.5 nm) corresponds to neutral donor-bound exciton transition, labeled as $I_2(D^0,X)$. The exciton nature of first two PL bands was confirmed by corresponding peculiarities in reflection spectra[6]. The $I_2(D^0,X)$ PL peak was identified to be caused by Ga_{Zn}[9]. The peak at 446.8 nm labeled as I_V^0 at 2.772 eV as well as the band Y_0 at 476.5nm were related to extended defects[10]. It should be noted that intensity of I_V^0 and Y_0 relatively to I_{FX} for thick (t>1 μm) ELs increases with its thickness. For the thick samples bands I_4=2.48 eV and I_5=2.21 eV in the deep-level energy region are observed in addition to described peaks. The I_5 band may be identified as donor-acceptor pair emission ($D\text{-}V_{Zn}$), the donor of the pair being the group I element (Li_i or Na_i). The band I_4 originates from the intrinsic defects in the ELs[11].

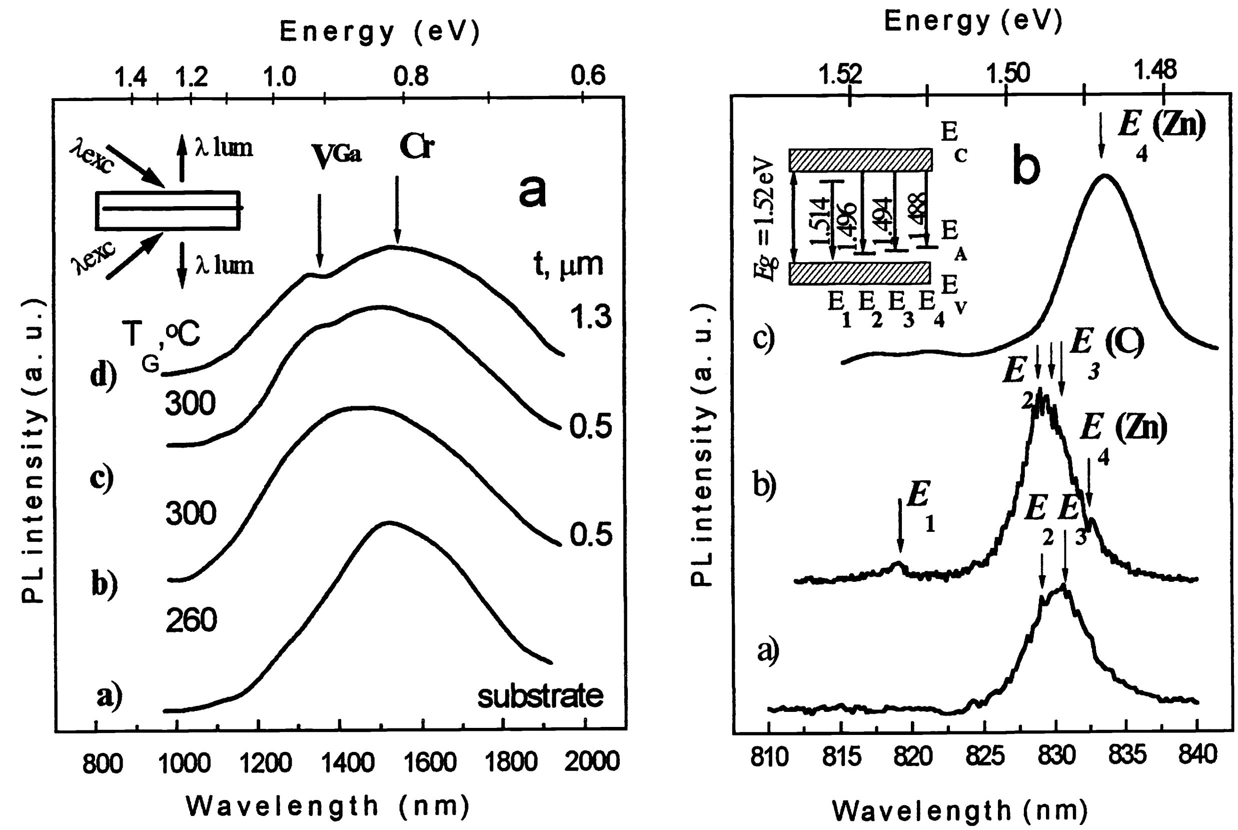

Fig.2, a. 77 K photoluminescence spectra of GaAs substrate taken from the back side (a) and through the ZnSe window (front side) (curve b,c,d) . λ_{EXC}=628.8 nm, P_{EXC}=8 W/cm^2.

Fig.2, b. 4.2 K photoluminescence spectra of GaAs substrate taken from the back side (a) and through the ZnSe (b) and $Cd_{0.28}Zn_{0.72}Te$ (c) window (front side) (curve b,c,d) . λ_{EXC}=632.8 nm, P_{EXC}=8 W/cm^2.

The spectra of thinner samples differ from ones of thick samples and show only the peak at 443.5 nm (Fig. 1, curve a). The full width on half maximum, FWHM, of these peaks varies from W=1.75 nm to W=1.07 nm for different samples grown under various technology conditions. All thin samples show a broad band I_6 at λ=620 nm. This band is the self activated luminescence connected with donor-acceptor pairs $D\text{-}V_{Zn}$, where donor is the group III element[11]. The absence of the exciton peculiarities in the reflection spectra of the most thin samples and large value of W for PL peak (Fig.1) testify to its band-to-band recombination nature. This conclusion is in agreement with high carrier density ($n \approx 8 \cdot 10^{17}$ cm^{-3} ÷ $1.3 \cdot 10^{18}$ cm^{-3}) which corresponds to degeneration. With increase of EL thickness the ratio of the donor bound exciton peak intensity to that of free exciton peak, I_2/I_{FX}, decreases. So we supposed that main back ground donor impurity in our ELs is Ga_{Zn} and that the source of Ga is GaAs substrate rather than the contamination of ZnSe ELs from equipment[9]. Really, the highest free electron concentration ($n \approx 1.3 \cdot 10^{18}$ cm^{-3}) was observed in the 0.5 μm thick samples grown on the Ga-rich substrates. However, the doping of ZnSe layers with Ga can be also observed when GaAs substrate doesn't Ga enriched[6]. This is confirmed by PL measurements of GaAs substrate and step etched ZnSe ELs.

Fig.2, a shows the deep-level region of the PL spectra of GaAs substrate of ZnSe/(001)GaAs samples with different EL thicknesses taken at 77 K under excitation by 0.6328 μm - line of He-Ne-laser through the ZnSe window (front side) (curve b,c,d) and from the back side (curve a). PL spectra of GaAs substrate excited from the back side practically are the same for all the samples and exhibit in the region 1000-2000 nm the band connected with Cr complexes (0.8÷0.84 eV)[12]. PL spectra of GaAs substrate excited from the front side show an additional shoulder near by 0.93 eV which was attributed to V_{Ga}[13]. It is seen that intensity of this band increases with the increase of sample thickness (t) and growth temperature (T_G). So the intermediate GaAs layer near heterointerface are riched by V_{Ga} which is obviously due to Ga diffusion into ZnSe layer.

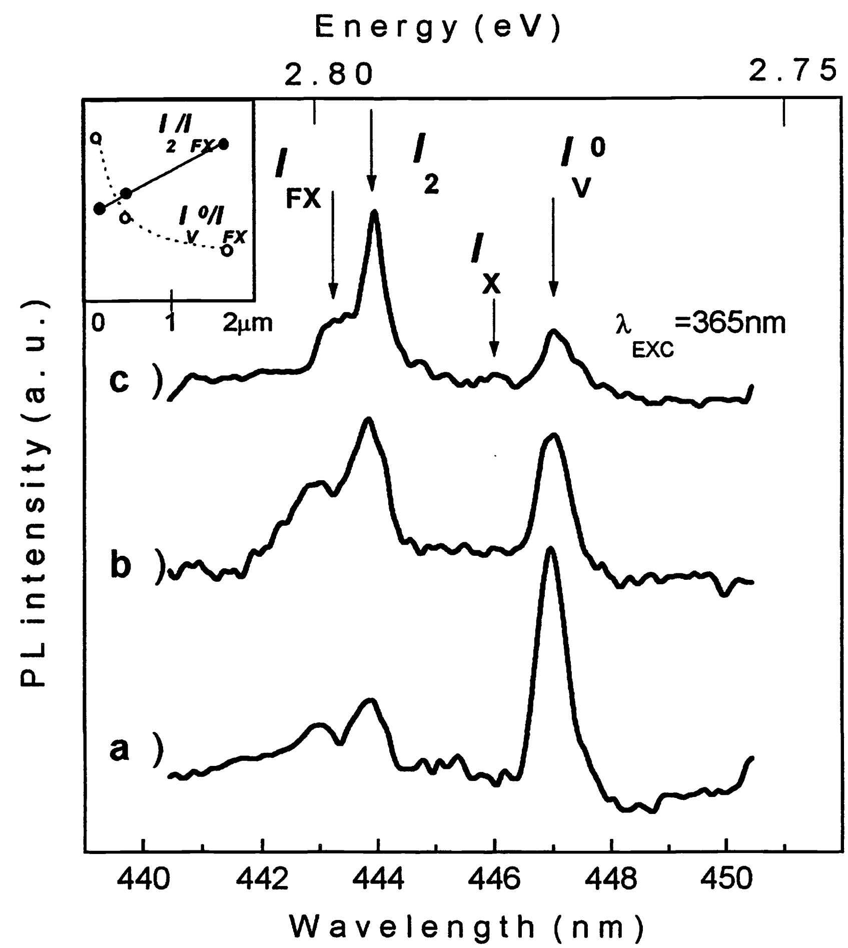

Fig.3. 4.2 K photoluminescence spectra of 2 μm thick ZnSe film: a) unetched, b) etched down to 1.8 μm, c) etched down to 1.3 μm. The inset shows the peak heights of I_2^{Ga} and I_V^0 normalized by height of I_{FX} as a function of depth in the ZnSe epilayer.

The investigation of the GaAs substrate PL spectra also give the evidence of Zn diffusion through the heterointerface. Fig.2, b shows the typical 4.2 K PL spectra from front and back sides of the GaAs substrate in the near-band edge emission of 1.3 μm ZnSe/GaAs. The bands E_3 and E_4 were identified as radiative capture of the electron to neutral carbon (E_3) and zinc (E_4). The presence of bands connected with the C_{As} on front (curves b,c) and back (curve a) sides of GaAs shows that C_{As} is the main background impurity in GaAs wafer. PL peak due to Zn_{As} from back side have not been observed (Fig. 2,a). Therefore we can conclude that E_4 band is the result of Zn diffusion from interface to GaAs during ZnSe growth.

Besides the nonuniform distribution of point defects the depth inhomogenious of extended defect location is observed also. X-ray measurements under step etching show that (004) rocking curve FWHM increases with the decrease of layer thickness that is obviously due to increase of extended defect density. The X-ray double-crystal topograms obtained from (311) asymmetric reflection of non-etched samples gives the additional information about EL inhomogeneity. We point out the existence of two regions with higher defect density: the thin near top surface region and near interface one. The last is of about 0.5 μm and contains high misfit dislocations and defect density. In the thin samples dislocations are present in the whole ZnSe layer volume.

PL data confirm the conclusion about the inhomogeneity of ZnSe ELs. Fig.3 shows 4.2 K PL data from the 2 μm ZnSe EL before (curve a) and after (curves b, c) step etching. After 0.2 μm etching the ratio I_2/I_{FX} changes insignificantly, while I_V^0/I_{FX} decreases. The etching of the 1.5 μm layer leads to increase of I_2/I_{FX} and decrease of I_V^0/I_{FX} ratios. PL spectra transformation at step etching allow to make the next conclusions: (i) I_2/I_{FX} ratio increases for near interface region which is in agreement with our assumption about Ga diffusion from GaAs substrate; (ii) I_V^0/I_{FX} ratio behavior shows the increase of extended defect or dislocation density in near top surface region.

The increase of I_V^0 intensity relatively to I_{FX} with epilayer thickness in thick samples (Fig.1, curves b,c) indicates the increase of epilayer deterioration in the near top region with the thickness rise. This is in agreement with non monotone FWHM of X-ray rocking curves dependence on layer thickness[6].

3.2 ZnTe and CdZnTe

Fig.4 shows the PL spectra of ZnTe ELs grown on the GaAs substrate with surfactant ZnTe intermediate (5 nm thickness) layer. They consist of free exciton band (λ=520.2 and 521.2 nm), exciton bound to donor, probably Ga (D^0X) (λ=522 nm) and emission lines of acceptor bound excitons (A^0X) (λ=523.4 and λ=526.0-526.24 nm) labeled as I_{FX}, I_2, I_1' and I_1^C, respectively. I_1' line was attributed to a neutral acceptor center in a strong trigonal crystal field, to a complex of simple acceptor and isoelectronic impurity (A_{Zn}-I_{Te} or A_{te}-I_{Zn}) or an A-center which consists of a zinc vacancy (V_{Zn}) and donor impurity from either group III or VII[14]. From a much stronger temperature dependence that FE peaks the authors[15] suggested it to be weakly bound exciton acceptor complexes ($A_A°$, X), $A_A°=A_s°$. The ratios of the I_2 (I_1') to I_{FX} intensity for λ_{exc}=0.4880 μm are approximately the same in samples grown with and without surfactant layer. The CdZnTe EL PL spectra in the exciton region show the bound exciton band only (Fig.5, curve b)[16]. Since the I_2 emission was identified as radiative recombination of exciton bound to substitutional Ga (Ga_{Zn}) we conclude that even the presence of intermediate ZnTe layer doesn't block the impurity diffusion through the interface. Ga-Zn interdiffusion through the interface is confirmed by GaAs substrate PL measurements through the CdZnTe wide gap window (Fig. 2, curve c) like in the case of ZnSe ELs as was mentioned

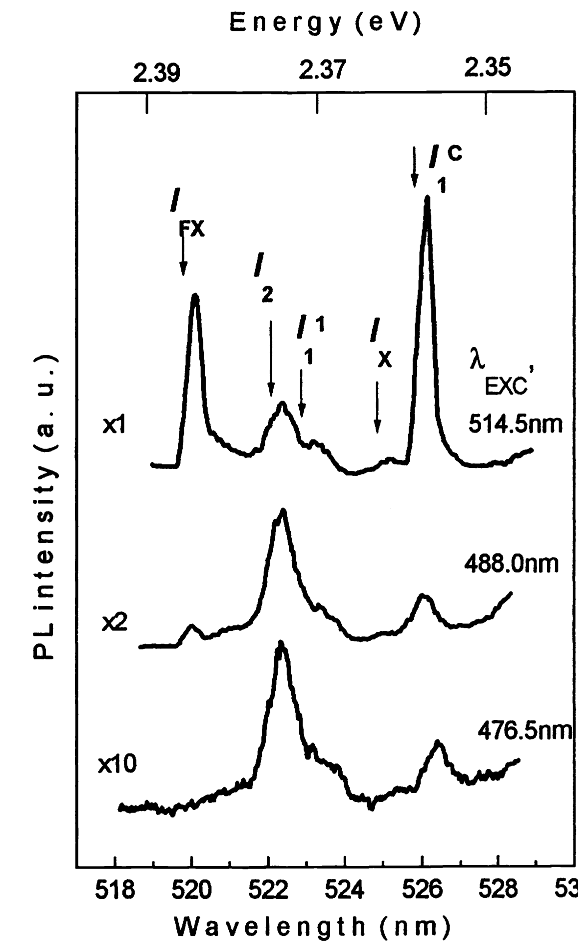

Fig.4. Exciton range of the 4.2 K photoluminescence spectra for the ZnTe epilayer excited with three different Ar^+ laser lines. P_{EXC}=8.3 W/cm^2.

previously. The increase of PL excitation wavelengths from λ_1=0.4765 μm, λ_2=0.4880 μm to λ_3=0.5145 μm result in the decrease of the ratio I_2/I_{FX} ($I_1^{\,l}/I_{FX}$) from about 10 (5) to about 0.5 (0.2) (Fig.4), respectively. This fact is the evidence of Ga and Zn accumulation on the top surface of ZnTe ELs that is in agreement with results of other authors[17].

In spite of the heterodiffusion of II-VI/GaAs heterosystem components is well known, it mechanism is not established exactly. Earlier[18] we observed formation of intermediate layer between the epitaxial film and substrate in closely matched Ge/(001) GaAs heterosystem grown by MBE at $T_G \approx 400°C$. Secondary ion mass spectrometry, SIMS, experiments show the outdiffusion of Ga and As from substrate to Ge film and noticeable increase of Ga concentration in the near top region of Ge films[19]. We assumed that (i) Ga atoms are accumulated in the near-surface region by "the pushing out" Ga by growing layer and have a peak at top surface[19]; (ii) Ga distribution in near interface region is determined by thermal diffusion of Ga atoms from substrate. It is obviously that analogous processes take place in the II-VI-GaAs systems grown by MBE, but the presence of mismatch between these materials can accelerate outdiffusion of components if the blocking techniques are no effective. We have used stoichiometric or As-rich GaAs wafers in the case of ZnSe/GaAs MBE ELs and intermediate solid phase crystallized ZnTe layer in the case of ZnTe and ZnCdTe ELs, but such substrate preparation was not an effective method for blocking of interdiffusion.

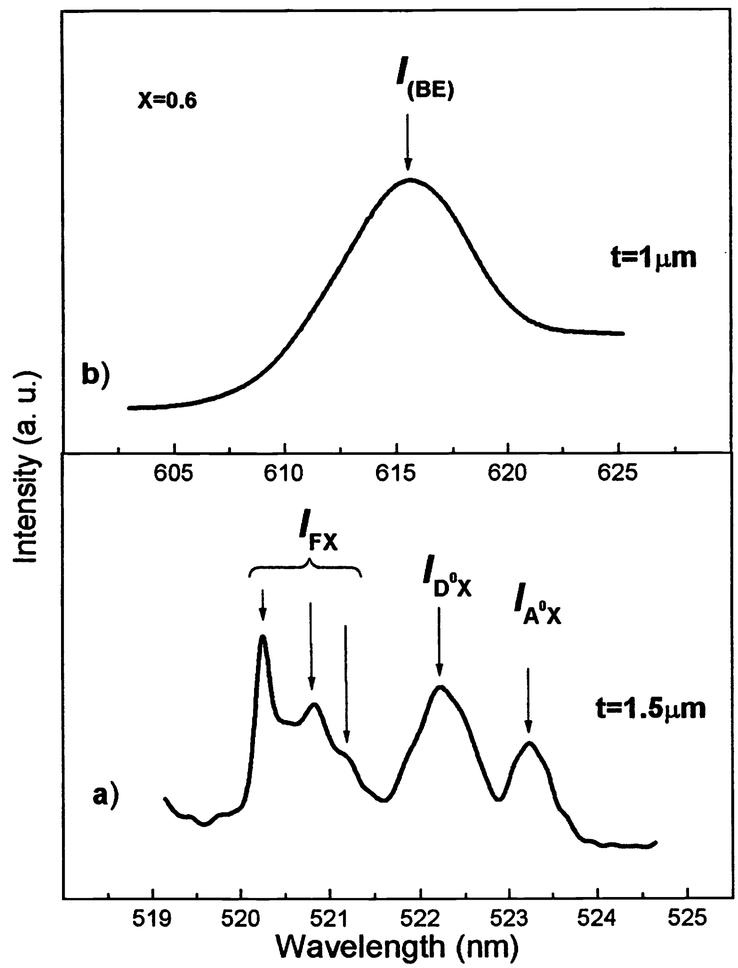

Fig. 5. Near band edge PL spectra at 4.2 K for ZnTe/GaAs (a) and $Cd_{0.4}Zn_{0.6}Te$/GaAs (b) epilayers. λ_{EXC} = 514.5 nm. P_{EXC}=8.3 W/cm^2.

In conclusion, the investigations of X-ray diffraction and PL spectra of thick ELs, ZnSe and ZnTe, under step etching and at different excitation wavelengths show that these ELs are depth inhomogeneous and consist of three region with different extended defect and impurity concentration: (i) near the interface region with high density of misfit dislocations and impurity concentration; (ii) the region with low extended defect and impurity concentration and (iii) near the top surface region with higher extended defect concentration. The last region for ZnTe EL, as well as for ZnSe ELs[20], was found to contain higher Ga_{Zn} concentration, i. e. two regions in EL with enhanced Ga concentration are present. These results can be explained by two-step process of Ga-diffusion from substrate: equilibrium Ga diffusion into the layer bordering on the substrate and subsequent "pushing out" Ga by growing layer.

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