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Defects and radiation-enhanced defect reactions in ZnSe/(001)GaAs MBE layers

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Abstract. Optical and structural properties of undoped ZnSe epilayers with thickness ranging from 0.5 to 2 μm grown by molecular beam epitaxy on GaAs (001) substrates have been investigated by depth resolved optical and X-ray methods. It was found that the epilayers with thicknesses above some value (>1 μm) contain three regions of different structural and optical quality. It is shown that two of these regions (near top surface and near interface ones) contain higher defect density. The nature of luminescence line at 446.1nm (4.2 K) is discussed. It was found that the radiation enhanced defect reactions occurred in the top surface region of epilayer.

Keywords: MBE, ZnSe, photoluminescence, degradation.

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1. Introduction

In recent years, ZnSe-based II-VI heterostructures have been intensively investigated as the promising candidates for light-emitting devices in the blue-green spectral range. However, their application is still limited by degradation processes [1]. It is known that degradation rate depends on the density of dislocations generated on ZnSe/GaAs heterointerface. So, the buffer layer of thickness $h<h_C$ (h_C - critical thickness for strain relaxation by misfit dislocations which is 0.15-0.2 μm for ZnSe/GaAs) is used as a rule. From the other hand, it was shown [2] that decrease of the total thickness of ZnSe layers separated the GaAs substrate and the active layers results in the drop of thermal stability of heterostructures. Thus, investigation of ZnSe layer characteristics in dependence on their thickness is to be interesting.

In present work dependence of the structural and luminescence characteristics of ZnSe epilayers both on their thickness and as a function of depth has been investigated. As it will be shown the top region of thick (1.3÷2 μm) epilayers contains the higher concentration of the extended defects and plays a noticeable role in radiation enhanced defect reaction.

2. Experiment and samples treatment

Five series of undoped ZnSe layers of different thickness (0.5-2 μm) were grown by molecular beam epitaxy (MBE) on semiinsulating Cr-doped oriented 3° off (001) towards [110] GaAs substrates in a CATYN' machine equipped with conventional effusion cells for Zn and Se. The residual pressure in the chamber was $\sim 8 \cdot 10^{-11}$ Torr. For deoxidation the GaAs substrates were heated up to the temperature of about 580 ^{0}C without or with the use of an As beam. Before the deposition of ZnSe epilayer the GaAs surface was treated in Zn flux during 100 s at pressure $\sim 4 \cdot 10^{-7}$ Torr for prevention the chemical reaction of Se and the excess Ga on the GaAs surface. Reflection high-energy electron diffraction, RHEED, was applied to control the surface during deoxidation and deposition processes. ZnSe epilayers were grown at the temperatures of 260–340 ^{0}C and Se/Zn beam pressure ratios were 1.2–1.5. The growth rate was ~0.6 μm/hour. The free carrier concentration, n, and mobility, μ, were obtained from Hall effect measurements at 300 K. Table 1 shows some technological conditions of the growth process and parameters of the samples.

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Table 1. Technology conditions and initial parameters of ZnSe epilayers.

Sample	Technology conditions			Epitaxial film			
No	Se/Zn ratio	T_g, °C	Surface reconstruction	Thickness, μm	n_{300K}, cm^{-3}	Mobility μ_{300K}, $cm^2/V{\cdot}s$	Zn or Se riched surface
50	1.2	300	c(2x2)	2.0	*	*	Zn
11	1.2	300	c(2x2)	1.3	*	*	Zn
34	1.2	300	c(2x2)	0.5	$8{\cdot}10^{17}$	220	Zn
35	1.2	260	(2x1)	0.5	$1.3{\cdot}10^{18}$	190	Se
36	1.5	340	c(2x2)	0.6	$2.1{\cdot}10^{17}$	250	Zn

*** high resistivity**

X-ray diffraction methods and X-ray topography as well as exciton and impurity luminescence spectroscopies were used to control the epilayer properties. Photoluminescence (PL) of ZnSe was excited by 365 nm line of the 200 W mercury lamp. PL spectra were recorded in the temperature range 4.2-77 K using the grating spectrometer MDR-23. Depth uniformity of ZnSe epilayers (ELs) was investigated using step etching. For simulation of the degradation processes the samples were subjected to the illumination by UV light of 500 W mercury lamp.

3. Experimental results and discussions

The (004) rocking curves for ZnSe/GaAs epilayers of different thickness grown under approximately the same conditions (T_g=300 ^{0}C, Se/Zn beam pressure ratio ~1.2) are shown in Fig.1. The angle between the ZnSe and GaAs (004) reflections increases with the increase of layer thickness. Using the angle value, the ratio of the out-of plane lattice parameter $a_\perp$ to in-plane lattice parameter $a_\parallel$ $a_\perp/a_\parallel$<1 was obtained, and a small residual biaxial tensile strain component was evaluated ($\varepsilon \leq 2{\cdot}10^{-3}$) for all the series of the samples. It is known that at 300 K the mismatch ~ 0.27 % between ZnSe and GaAs ($a_{ZnSe} > a_{GaAs}$) should result in the in-plane biaxial compressive strain. Since all investigated samples were grown of thickness $h > h_C$ a partial strain relaxation is expected to occur during the growth processes [3, 4]. Therefore, small tensile strains observed at 300 K are the thermally induced strains stemming from different thermal expansion coefficients of the ZnSe epilayer and the GaAs substrate [3].

The (004) rocking curves full width at half maximum (FWHM) changed nonmonotonically with the increase of layer thickness (Fig.1). The narrowest curve was obtained from the 1.3 μm thick films that demonstrates a crystalline quality of such epilayers.

An additional information about the epilayer quality was obtained from PL data. The PL spectra of the investigated ZnSe ELs at 4.2 K are shown in Fig. 2. The spectra of thick samples (curves 2, 3) in the near band edge region consist of the narrow bands at λ_{m1}=442 nm, λ_{m2}=443.5 nm, λ_{m3}=446.8 nm and λ_{m4}=476.5 nm. The position of first peak corresponds to free-exciton transition, I_{FX}. On the more large scale it consist of two peaks (main peak and shoulder at shorter wavelengths). This double peak can be ascribed to valence band splitting on light-hole, lh, and heavy-hole, hh, branches due to strain [3]. Position of the second PL peak corresponds to neutral donor-bound transition, I_2 (D^0, X). The I_2 (D^0, X) peak is attributed usually to Ga_{Zn} [5,6].

The band at 446.8 nm labeled as I_V^0 was attributed to extended defects [7-9] as well as the band Y_0 at 476.5 nm [7]. On the short wavelength side of I_V^0 peak the shoulder or the peak at 446 nm (I_X) is often observed in our samples also (see Fig. 4). Spectral position of last peak is close to the positions of two-electron satellite (2EL) of

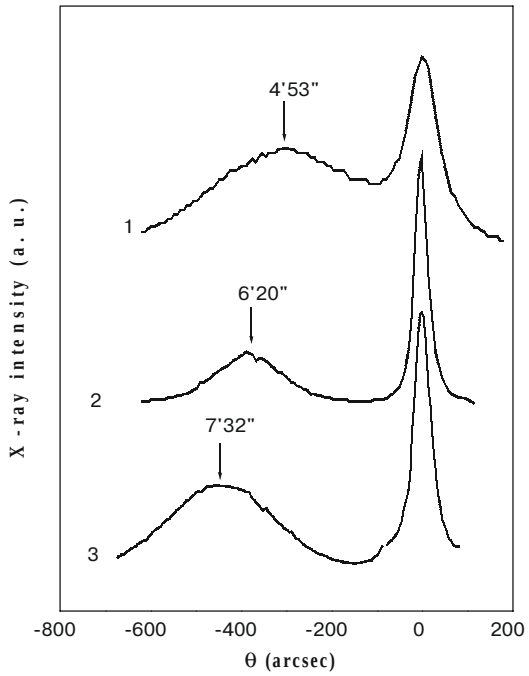

Fig. 1. (004) X-ray diffraction curves of ZnSe epilayers of different thicknesses: 0.5 (curve 1), 1.3 (2) and 2.0 μm (curve 3).

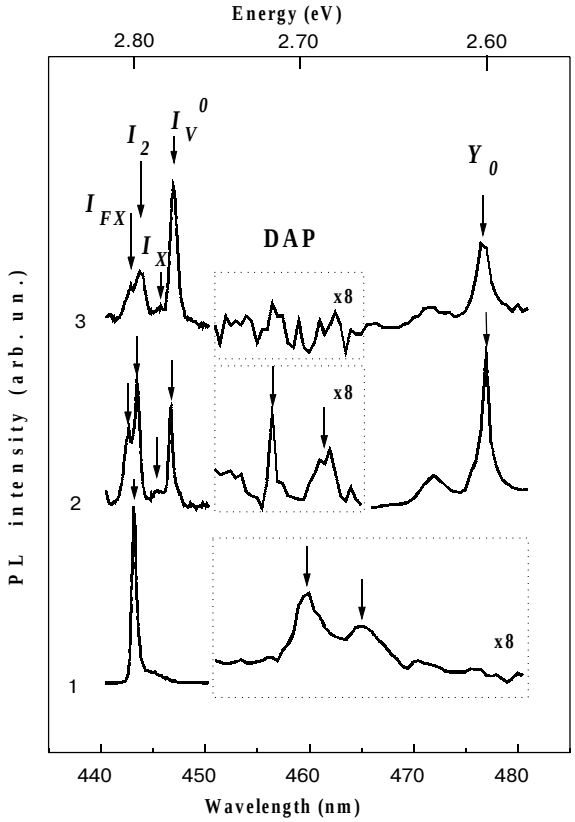

Fig. 2. Typical 4.2 K photoluminescence spectra from ZnSe epilayers of different thicknesses: 0.6 (curve 1), 1.3 (curve 2) and 2.0 μm (curve 3) λ_{exc}=365.0 nm.

(D^0, X) transitions and neutral acceptor bound exciton (connected with As or its complexes) [3]. Its possible nature will be considered later. In the spectral region between I_V^0 and Y_0 bands the weak luminescence of different DA-pairs, namely DAP-1 (456.5 nm), Q-DAPs (460-461 nm) and DAP-2 (462 nm), are observed [10].

In the 500-700 nm spectral region the PL bands connected with deep level defects are observed in all the samples. For the thick layers weak PL bands were observed at 500 nm and 560-580 nm (DAP) [10] while PL spectra of the thin samples showed a broad peak at 620 nm. The latter one is due to donor-acceptor pairs V_{Zn}-D, where D is the group III element [10].

The low value of ratio of donor bound exciton peak intensity to that of free-exciton $\xi \approx 1$ ($\xi = I(D^0,X)/I(FX)$) in our thick epilayers confirms their high optical quality. It should be noted that intensity of I_V^0 and Y_0 relatively to I_{FX} increases when epilayer thickness increases from 1.3 to 2 μm (Fig. 2, curve 2, 3). The increase of I_V^0 intensity relatively to I_{FX} and I_2 with epilayer thickness shows the deterioration of epilayer when its thickness is above some optimal value. This is in agreement with nonmonotonical dependence of FWHM of X-ray rocking curve on h.

The PL spectra of thinner samples (No 34-36, see Table) show the peak at 443.5 nm only (Fig. 1, curve 1). The FWHM of these peaks varies from 7 meV (sample No 36) to 11 meV (sample No 34). Optical reflection spectra contained the excitonic peculiarities for the sample No 36 only. The absence of the exciton peculiarities in the optical reflection spectra and large FWHM of PL peak in samples No 34 and 35 testify to its band-to-band recombination nature that is in agreement with high carrier density obtained from Hall measurements. Presence of the I_2 peak in samples No 50, 11 and 36 indicates diffusion of Ga from the substrate to ZnSe epilayer [5]. We think that high carrier concentration in samples N34, 35 is connected with Ga_{Zn} also because the highest free electron concentration is observed in the sample №35, which is grown on the Ga-riched substrate. So, PL measurements show the higher quality (lower impurity concentration) of thick samples comparing to thin ones that is in agreement with results obtained in [11].

PL spectra transformation at step etching revealed considerable depth inhomogeneity of 2 μm thick sample that was characterized by high value of FWHM of rocking curve. Fig. 3 represents 4.2 K PL spectra before (curve 1) and after (curves 2, 3) step etching of sample. After 0.2 mm etching an intensity of I_V^0 line decreases essentially. At the same time the ratio I_2/I_{FX} changes insignificantly. Etching of the 1.5 μm layer leads to subsequent decrease of I_V^0/I_{FX} and to increase of I_2/I_{FX} ratios (inset in Fig.3). It is known that I_V^0 intensity drops with the increase of impurity concentration [12], that may be the reason of I_V^0 intensity drop after etching. But insignificant change of I_2/I_{FX} ratio after 0.2 μm layer etching testifies to that I_V^0 decrease is due to not the change of Ga concentration but to the decrease of extended defect concentration. So, we can conclude that the top region of thick epilayers contains higher extended defect concentration.

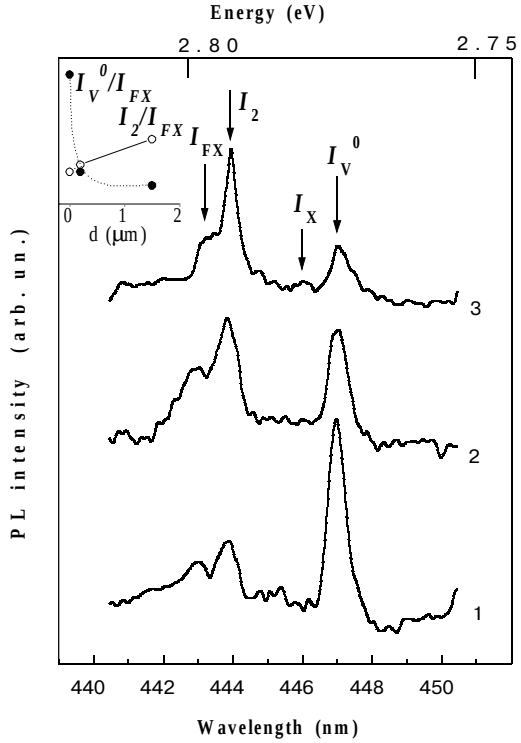

Fig. 3. 4.2 K PL spectra of thick 2.0 μm ZnSe epilayer: unetched (curve 1), etched down to 1.8 μm (curve 2), etched down to 1.3 μm (curve 3), λ_{exc}=365.0 nm. The inset shows the I_2^{Ga} and I_V^0 peak intensities normalized by height of I_{FX} line as a function of depth (d) in the ZnSe epilayer.

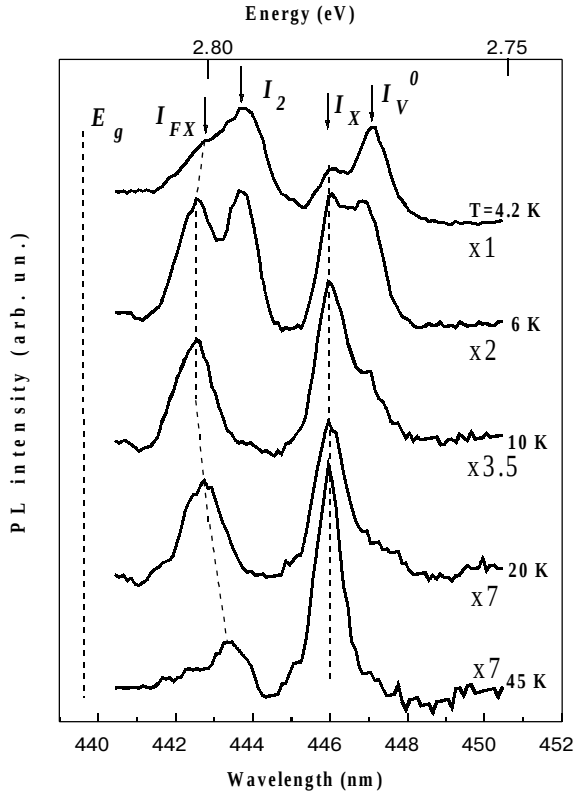

Fig. 4. Temperature transformation of the excitonic photoluminescence of 1.3 μm ZnSe epilayer, λ_{exc}=365 nm.

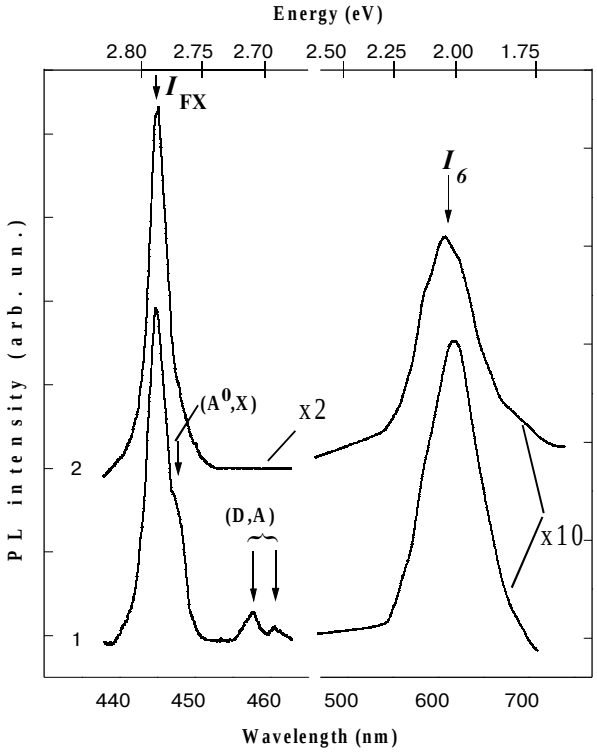

Fig. 5. 77 K PL spectra of 0.6 μm ZnSe epilayer before (a) and after (b) UV irradiation λ_{exc}=365 nm.

The X-ray measurements fulfilled on 2 μm thick ZnSe epilayer under step etching confirmed the depth inhomogeneity of the ZnSe epilayers. The X-ray double-crystal topography of the samples gives an additional information about this inhomogenity. The topograms were obtained from (311) asymmetric reflection before and after etching. From these experimental results we point out the existence of two regions with higher defect density: thin near top surface region and near interface one. The latter has the thickness ~ 0.5 μm and contains high misfit dislocation and point defect density. PL spectra confirm this assertion. Increase of the I_2 peak intensity in comparison with I_{FX} one after 1.5 μm layer etching is in agreement with supposed donor nature (Ga_{Zn}) of this peak (diffusion from GaAs substrate). It should be noted that in the thin samples dislocations are present in the whole ZnSe layer volume.

Let us consider now the possible nature of I_X band. It is essential that the high ratio (~0.3) of I_X/I_2 intensities can be observed in our samples (Fig. 4). This fact testifies against the two-electron satellite of (D^0, X) nature of I_X. To get an additional information about the I_X band we investigated the temperature dependence of PL spectra of the thick samples. As figure 4 shows the temperature dependence of I_X intensity does not correlate with the same dependencies for I_2 and I_{FX}. This fact does not allow us to suppose that I_X is the I_2 satellite or acceptor bound exciton. This is confirmed by the absence of corre-

lation between the temperature dependence of I_X and I_{FX} band maximum positions: I_X band position does not change practically up to T = 45-50 K whereas FX position shifts toward the low energies. Such temperature dependencies of I_X intensity and peak position in conjunction with its small FWHM are typical for PL lines connected with dislocations in II-VI compounds [13].

For elucidation of the top imperfect layer contribution in degradation processes we investigated the influence of UV-radiation on its PL characteristics. Fig. 5 shows the 77K photoluminescence spectra from ZnSe epilayers before (curve 1) and after UV-irradiation (curve 2) (sample N36). The near band edge emission at this temperature shows the combination of band I_{FX} and shoulder at 447 nm. The last PL band was identified as exciton bound to neutral acceptor (A^0,X) caused by V_{Zn} [10]. In addition a weak structural donor-to-acceptor (D,A) band connected with Ga (450-480 nm) and the one connected with V_{Zn}-Ga_{Zn} (620 nm - I_A) are observed. After UV irradiation within 3 hours at room temperature (D,A) band disappears completely (Fig. 5, curve 2). The intensity of the (A^0,X) band as well as the I_A band decreases as the time of treatment increases. This fact gives the evidence that UV light enhanced point defect reactions including Ga_{Zn} and $V_{Zn.}$ take place in the investigated layers. Because the UV light is absorbed in the near surface region (~ 0.1 μm) the observed point defect reactions take place in the near top part of epilayer.

4. Conclusion

In conclusion, we have found that increase of epilayer thickness up to 1.3 μm results in the increase of its structural quality and decrease of impurity concentration. However, further increase of epilayer thickness leads to epilayer deterioration. Besides, we have shown that the thick samples 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 point defects; (ii) the region with low extended defect and impurity concentration and (iii) near the top surface region with higher extended defect concentration. Experiment on step etching and temperature dependence of PL spectra allow us to conclude that I_X line (λ=446 nm) is connected with extended defects (dislocations).

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