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Emission Associated with Extended Defects in Epitaxial ZnTe/GaAs Layers and Multilayer Structures

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Abstract—It was shown by the methods of X-ray diffraction and photoluminescence that the use of a thin intermediate recrystallized ZnTe layer between the ZnTe buffer layer obtained by molecular-beam epitaxy and GaAs substrate, as well as an increase in the thickness of the epilayer result in the improvement of the structure (enhancement of the mosaic size) and an increase in the intensity of exitonic bands. It is established that a number of characteristics of the I_1^C bands with $h\nu \approx 2.361$ eV, which are observed in the samples with quantum wells and superlattices, differ from the corresponding features of the emission lines of free and bound excitons and those lines typical of dislocation-related radiation in II–VI single crystals. It is assumed that the I_1^C band is associated with the subblocks boundaries, which comprise the mosaic structure of epitaxial layers. © *2000 MAIK "Nauka/Interperiodica".*

INTRODUCTION

It is known that, during the growth of epilayers of II–VI semiconductors on GaAs substrates, a transition layer with high densities of dislocation and other extended defects [1] is formed; these defects affect the optical properties of epilayers and also stimulate the degradation processes in light-emitting diodes fabricated on the basis of these layers [2]. This makes the problem of the identification of the bands associated with extended defects (dislocations among them) urgent in II–VI epilayers.

It is known that, in photoluminescence (PL) [3] and cathodoluminescence spectra [4] of ZnTe epilayers obtained by various methods, as well as of single crystals [5], an intense emission line I_1^C is often present ($h\nu = 2.357$ eV at 4.2 K) [6]. It is assumed that this line is caused by the radiative recombination of excitons bound either with the isolated neutral acceptor (Si_{Te} [5]), or with the acceptor (V_{Zn}) located near the misfit dislocation (vacancy-dislocation complex) [3, 7]. Thus, the nature of this band has not yet been finally established.

For elucidating the origin of emission centers responsible for the I_1^C band, the influence of buffer ZnTe epilayer on the PL spectra is studied in this work. In particular, we studied the effects of (i) a thin (~5–10 nm) intermediate recrystallized ZnTe layer placed between the buffer layer and (100) GaAs; (ii) the thickness of the buffer layer, as well as (iii) grown quantum-size layers of $Cd_xZn_{1-x}Te$/ZnTe ($x = 0.2$–0.4). In addition, the spatial distribution (over the thickness of the buffer) of the intensity (I) and spectral position (λ_m) of I_1^C band, as well as temperature dependences of I and λ_m were studied. The X-ray diffraction measurements of rocking curves were carried out simultaneously for monitoring the crystal perfection of ZnTe epilayers.

EXPERIMENTAL

All the structures were obtained by the molecular-beam epitaxy (MBE) in a Katun' setup by the evaporation of high-purity elements onto the semiinsulating (100) GaAs substrate. The GaAs surface was cleaned of the oxide layer by heating in a vacuum at a temperature of ~550–580°C; the state of the surface was monitored during the growth by the method of reflection high-energy electron diffraction (RHEED). The growth of ZnTe layers was carried out by two methods. In the first method (process I), after the substrate was cooled to the temperature of 250–280°C, molecular beams of zinc and tellurium were delivered simultaneously with to the substrate the ratio of their equivalent pressures $I_{Zn}/I_{Te} = 1 : 2$. This results in the reconstruction of the surface $a(2 \times 1)$, i.e., to its stabilization by tellurium. After film grew up to tens of nanometers, the temperature was increased up to $T_G \approx 350$°C. The epitaxy was carried out at this temperature and at the ratio of Zn/Te beam intensities to provide a simultaneous coexistence of reconstructions $a(2 \times 1)$ and $c(2 \times 2)$ for the fulfillment of growth conditions close to stoichiometric.

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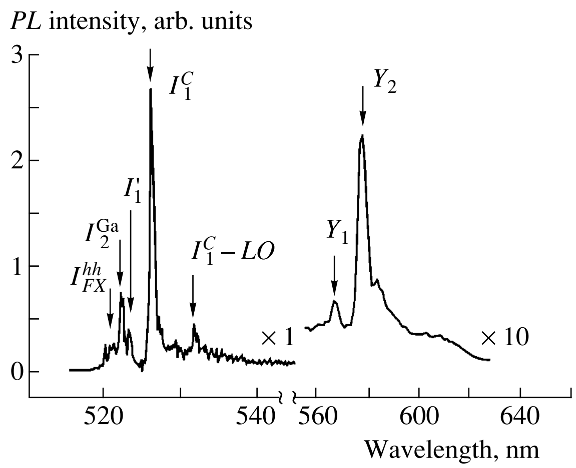

Fig. 1. Photoluminescence spectrum at T = 4.2 K of undoped buffer ZnTe/GaAs epitaxial layer 1.5 μm thick, grown with a thin intermediate recrystallized layer, λ_{exc} = 0.488 μm and P_{exc} = 8.3 W/cm^2.

In the second method, an intermediate amorphous ZnTe layer was deposited onto the substrate to improve the growth conditions [4]; then this layer was crystallized in the Te flow at T = 400–450°C. After crystallization, the substrate was cooled to 250–280°C and afterwards all the growth procedures described for process I were successively carried out.

PL was excited by the Ar^+-laser at the wavelengths λ_{exc} of λ_1 = 0.448 μm and λ_2 = 0.5145 μm and was measured at temperatures 4.2–77 K by the grating spectrometer with a resolution of ~0.5 meV. The layer-by-layer etching (in a solution of Br_2, HCl, and dioxane [8]) was used for studies of the distribution of radiative-recombination centers over the thickness of the layers. Some initial parameters of samples are listed in the table. The X-ray rocking curves were measured for studies of defect structure of layers on a two-crystal diffractometer [8].

EXPERIMENTAL RESULTS

3.1. Dependence of PL Spectra on the Preparation Conditions and Thickness of Layers

A typical spectrum of PL for ZnTe/GaAs buffer epilayer (see table, sample 2) at 4.2 K in the wavelength range of 510–630 nm is shown in Fig. 1. The spectrum involves the emission lines of free exciton (I_{FX}) split by the biaxial tensile stress into the following two components: I_{FX}^{hh} (X_{IS}; $m_j = +3/2$) and I_{FX}^{lh} (X_{IS}; $m_j = +1/2$) [3]. In this case, the line with $h\nu$ = 2.379 eV corresponds to

Parameters of samples under study

The sample no.	Buffer epilayer		Type of quantum-size layers		Position of PL bands for λ_m for λ_{exc} = 488 nm and T = 4.2 K			Half-width of rocking curves (in seconds of arc)	ε
	Thickness, μm	Type of process	Quantum wells	Superlattices	I_2^{Ga}, eV	I_1', eV	I_1^C, eV		
1	2.7	II	–	–	2.3747	2.369	2.357	~312	5.4×10^{-4}
2	1.5	II	–	–	2.3745	2.369	2.357	~360	5.6×10^{-4}
3	1.5	I	–	–	2.3734	2.37	2.356	~570	6.6×10^{-4}
4	1.5	II	$Gd_{0.3}Zn_{0.7}Te$ $L_{Z1} = L_{Z2} = L_{Z3}$ = 2 nm L_B = 30 nm	–	2.3741	2.3691	2.3569	–	6.4×10^{-4}
5	1.5	II	$Cd_{0.2}Zn_{0.8}Te$ L_Z = 5 nm	–	2.374	2.37	2.357	–	6.4×10^{-4}
6	1.5	II	$Gd_{0.3}Zn_{0.7}Te$ L_Z = 5 nm	–	2.3730	2.368	2.3565	–	6.5×10^{-4}
7	1.5	II	$Gd_{0.3}Zn_{0.7}Te$ L_{Z1} = 2 nm L_{Z2} = 4 nm L_{Z3} = 8 nm L_B = 30 nm	–	2.3734	2.368	2.357	–	6.9×10^{-4}
8	1.5	II	–	$Gd_{0.3}Zn_{0.7}Te$15 periods with L_Z = 2 nm L_B = 2 nm	2.3727	2.368	2.3557	–	7.3×10^{-4}

the I_{FX}^{hh} component, and the line with $h\nu = 2.374$ eV, to I_{FX}^{lh} component; the latter line is likely to be the superposition of I_{FX}^{lh} and the emission line of exciton bound with the neutral donor ($I_2^{\rm Ga}$) [3]. The line of exciton bound with the neutral acceptor (I_1') (presumably $\rm As_{Zn}$ [6] or a complex including $V_{\rm Zn}$ [9]) is also observed.

In addition to PL bands described, the intense band I_1^C peaked at $h\nu_m = 2.356$ eV and accompanied on the long-wavelength side by a nearby band with $h\nu_m$ = 2.352 eV (I_2^C) with lower intensity is observed in the excitonic region of the spectrum (Fig. 1). In the samples with quantum-size layers, on the short-wavelength side from I_1^C, the additional band I_X is observed with $h\nu_m$ = 2.359 eV (see table, samples 8 and 6) (Figs. 2a and 2b, respectively). The band I_1^C is apparently a composite one, because one can observe in some samples a clearly pronounced shoulder on its long-wavelength side (Fig. 2). The bands located placed near I_1^C are accompanied by the phonon satellites with the electron-phonon coupling factor $s \approx 0.2$ (Fig. 1). To the longer wavelengths, fairly less intense (as compared to I_1^C) bands Y_1 ($h\nu_{m1}$ = 2.189 eV at 4.2 K) and Y_2 ($h\nu_{m2}$ = 2.147 eV at 4.2 K) were observed.

The use of the intermediate ZnTe layer (process II), as well as an increase in the epilayer thickness, result in an increase in intensity of all lines in the excitonic region and in a decrease in the intensities of the impurity band (λ = 650 nm) and the bands Y_1 and Y_2. Both these bands are virtually absent for the layer thickness of ~2.7 μm. One should note that the ratios of band intensities $I_2^{\rm Ga}/I_{FX}^{hh}$ and I_1'/I_{FX}^{hh} remain virtually constant when we pass from sample 1.5 μm thick to sample 2.7 μm thick ($\lambda_{\rm exc}$ = 0.488 μm), whereas the ratio I_1^C/I_{FX}^{hh} slightly increases [8].

Along with the change of the bands intensities, a shift of their peaks is observed (see table). The positions of band peaks for free I_{FX}^{hh} and bound excitons $I_2^{\rm Ga}$ (I_{FX}^{lh}), I_1', and for I_1^C band are shifted towards lower energies as compared to their position in the bulk material ($E = 2.3805 \pm 0.0003$ eV, 4.2 K [10]); this is caused by the presence of plane tensile stresses ε [3]. In this case, the value of the shift is maximal in the samples obtained without the intermediate layer, and in the samples where the intermediate layer decreases as the epilayer thickness increases, which indicates that the stresses are relieved. Deposition of superlattice results in a noticeable shift of the peaks to lower energies, i.e., in an increase in tensile stresses, the values of which are

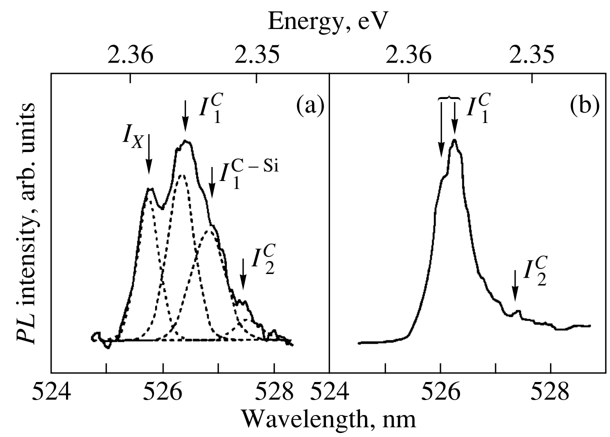

Fig. 2. Detailed PL spectrum in the 524–528 nm range of ZnTe/GaAs epilayer in the samples with a superlattice (a) and a single quantum well (b) at 4.2 K, $\lambda_{\rm exc}$ = 0.488 μm and $P_{\rm exc}$ = 8.3 W/cm^2.

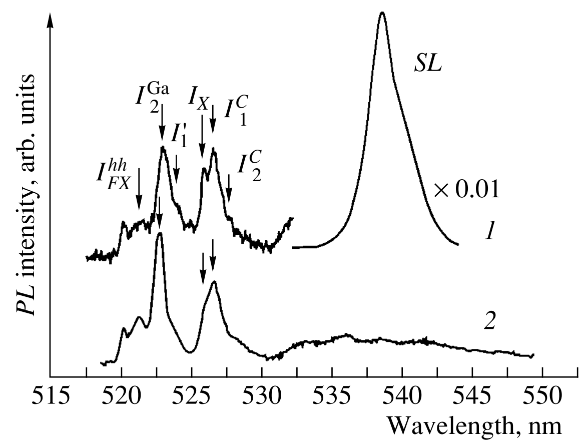

Fig. 3. PL spectrum of undoped buffer ZnTe/GaAs layer 1.5 μm thick with a superlattice prior (*1*) and after (*2*) etching off of the layer ~0.1 μm thick at $\lambda_{\rm exc}$ = 0.488 μm, $P_{\rm exc}$ = 8.3 W/cm^2, T = 4.2 K.

given in the table. The deformation-potential constants and the formulas given in [11] were used in calculations. It is noteworthy that the peaks of $I_2^{\rm Ga}$ and I_1' bands shift with the stress increase almost similarly, whereas the peak of the band I_1^C shifts to a lesser extent, which agrees with data from [11].

In [3], the band with I_1^C was assigned to an exciton bound with $V_{\rm Zn}$ near the dislocation, and it was assumed that the corresponding radiation comes predominantly from the GaAs–ZnTe interface region; therefore, we studied the distribution of I_1^C over the depth of the epilayer using the layer-by-layer etching of samples with the step of ~0.1 μm.

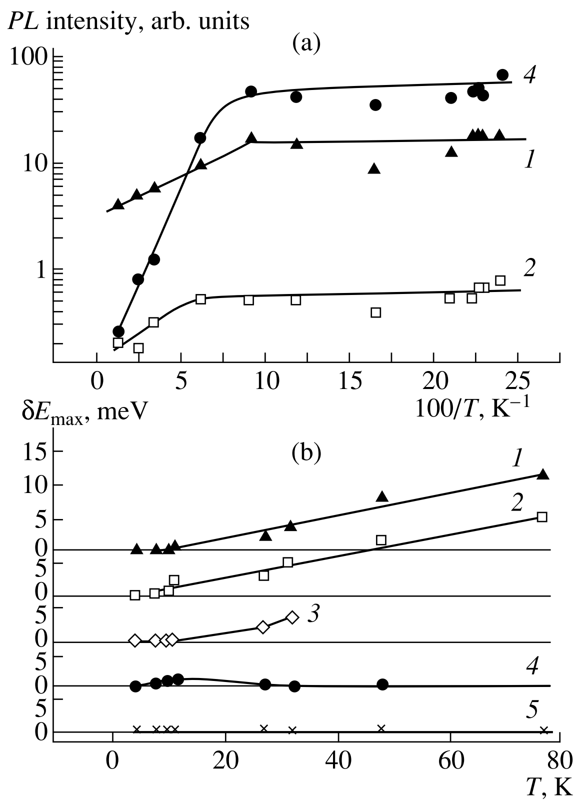

Fig. 4. Temperature dependences of intensity (a) and spectral shift of PL bands (b) in the 4.2–80 K range for ZnTe/GaAs epilayer with a single quantum well. The bands I_2^{Ga}, I_{FX}, I_1', I_1^C, and I_X are designated by *1–5*, respectively.

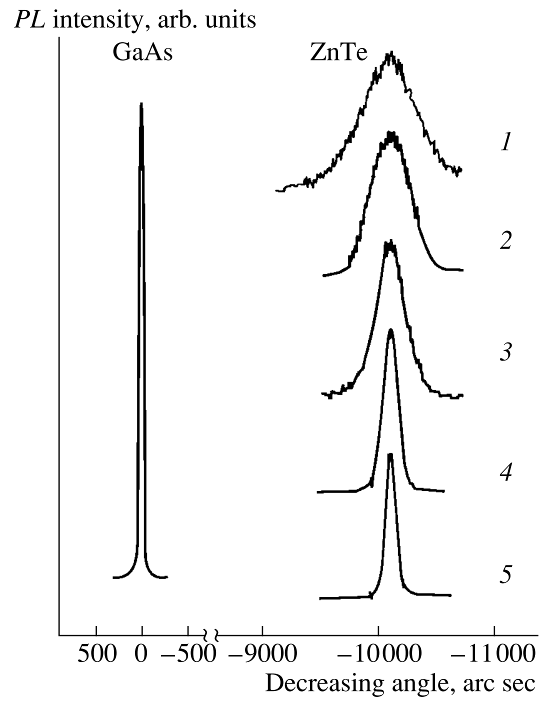

Fig. 5. Two-crystal X-ray diffraction rocking curves for ZnTe/GaAs epilayers of various thicknesses: (*1*, *2*) 1.5 μm; (*3*, *4*, and *5*) 2.7, 3.2, and 5.7 μm, respectively. For comparison, a GaAs substrate is shown (W = 36″). The rocking curves are arbitrarily shifted along abscissas for clarity. The (004) reflection and Cu$K_{\alpha 1}$ radiation was used.

As is seen from Fig. 3, the etching off of the layer ≈0.1 μm thick (see table, sample 8) results in a decrease in the relative intensities of bands $I_2^{\mathrm{Ga}}/I_{FX}^{hh}$, I_1'/I_{FX}^{hh}, I_1^C/I_{FX}, and I_X/I_{FX}^{hh}. In this case, the band I_2^{Ga} was shifted to shorter wavelengths, which was caused by a decrease in the magnitude of strain. The successive etching off of the layer ≈0.2 μm thick resulted in a decrease in the ratios $I_2^{\mathrm{Ga}}/I_{FX}^{hh}$, I_1'/I_{FX}^{hh}, I_1^C/I_{FX}, and I_X/I_{FX}^{hh}. The shift of I_X and I_1^C bands was not observed.

3.2. Temperature Dependence of the PL Spectrum

Figures 4a and 4b show the temperature dependences of intensities and temperature shifts of band peaks ($\Delta E_{\max} = h\nu_{4.2} - h\nu_T$, where $h\nu_T$ is the peak position of the corresponding band at temperature T) in the excitonic part of the spectrum for sample 5 (see table). As the temperature increases above 15 K, the intensity of all these bands begins to diminish. The intensity of I_2^{Ga} band varies similarly to the intensity of I_{FX}^{hh} band in this case. At the same time, the slope of temperature dependence for I_1^C in this temperature region (>15 K) is noticeably steeper and corresponds to the activation energy ΔE_a ~ 0.008 eV (Fig. 4a). Along with a decrease in the intensity of PL bands as the temperature is elevated, the spectral positions of free exciton I_{FX}^{hh} and bound exciton (I_2^{Ga} and I_1') emission lines are shifted to longer wavelengths with a thermal shift coefficient dE/dT ~ 0.16 meV/K in the temperature range of 20–80 K (Fig. 4b). At the same time, position of I_1^C and I_X lines practically do not change up to the temperature of 80 K.

3.3. Changes in X-ray Diffraction

The two-crystal rocking curves are shown in Fig. 5 for ZnTe epilayer of various thicknesses with the intermediate layer (curves *2–5*) and without it (curve *1*). The half-width of rocking curves (W) for ZnTe epilayer 1.5 μm thick without the recrystallized layer is ≈570″ (curve *1*, Fig. 5). The use of a thin recrystallized layer and an increase in the epilayer thickness from 1.5 to 5.7 μm resulted in a noticeable decrease in W from 312″ (curve *2*) to 90″ (curve *5*), respectively. It is known that for ZnTe/GaAs epilayer with a large mismatch of the layer and substrate lattice parameters

(f ~ 7.9%) for thicknesses exceeding critical values, the relaxation of stresses occurring by the introduction of misfit dislocations is followed by the formation of a mosaic structure [12]. The sizes of mosaic blocks (regions of coherent scattering) were increased from 0.065 (curve *1*) up to 0.75 μm (curve *5*).

DISCUSSION OF RESULTS

As is evident from the results presented, a number of characteristics of the bands I_1^C and I_X differ from those of both free and bound excitons. This difference manifests itself in the absence of a shift for the peaks of these bands in the temperature range of 4.2–80 K, and in a smaller, as compared to I_{FX}^{hh} and I_2^{Ga}, shift of λ_m when the strains are changed. The latter effect is evidenced by the dependence of positions of I_1^C and exciton lines on the presence or absence of the intermediate layer and epilayer thickness as well as by the shift of I_1^C and I_X bands as a result of the layer-by-layer etching of samples. One should note that a slight shift of the position of I_1^C with an increase in the epilayer thickness was observed also in [3] and was explained by assuming that the emission centers corresponding to this band are located predominantly in deeper layers adjacent to the ZnTe/GaAs interface. This made it possible [3] to relate the centers responsible for I_1^C band to defects in the neighborhood of misfit dislocations. However, as our experiments with the layer-by-layer etching of the epilayer show, the intensity of I_1^C band diminishes with the depth of the layer, which contradicts the assumption that the corresponding centers and misfit dislocations are related. It is important that the magnitudes of elastic strains decrease with an increase in the epilayer thickness, whereas the intensity of the I_1^C band increases. Such an anticorrelation of I_1^C and ε can indicate that this band is related to some extended defects, but not to the misfit dislocations. Another argument in favor of the relation of I_1^C and I_X bands to extended defects is the similarity of their characteristics with those of PL bands appearing in a number of II–VI single crystals after the low-temperature plastic deformation (so-called dislocation-related emission [13, 14]). Actually, as is shown in [13, 14], the plastic deformation of CdS, CdSe, and CdTe single crystals affects the bands in PL and optical absorption spectra. As in the case of the bands studied by us, the positions of the peaks of dislocation-related emission bands do not follow the temperature change of the forbidden gap width (the shift is absent up to ~40 K [13]), and also responds weaker to the mechanical stresses than the line positions for the free and bound excitons. The aforementioned similarity I_1^C and I_X to dislocation-related emission bands can be regarded as evidence for their common nature. A fairly large value of the Huang-Rhys factor s ~ 0.2, is apparently caused by the acceptor character of the state responsible for the I_1^C and I_X bands [13].

However, one should note that the dislocation-related emission in the bulk II–VI materials practically disappeared if they were kept at room temperature [13], whereas the I_1^C and I_X bands are the PL spectra of ZnTe epilayers which were retained without a time limit. This difference can be easily explained by the fact that the defects (impurities) mobile at room temperature are present in bulk materials and decorate the dislocations, which result in a decrease in the intensity of dislocation-related bands. At the same time, undoped ZnTe epilayers grown by MBE are much purer than single crystals. Such an explanation is consistent with the fact that the doping of the ZnTe epilayer by acceptor (nitrogen) and donor impurities (chlorine) significantly reduces the I_1^C band intensity, and this band is not detected at all for the impurity concentration $N > 10^{15}$ cm^{-3} [6].

In conclusion, we dwell on the detailed interpretation of I_1^C band as assigned to an exciton bound with the double-charged acceptor $\mathrm{Si_{Te}}$ [5]. The presence of a doubly charged acceptor was established by the Zeeman effect studies in the bulk of ZnTe single crystals [5]; the emission line 524.96 nm (E = 2.36308 eV) at 5 K corresponds to this acceptor. In the case of ZnTe epilayers obtained by various methods, MBE among them, the line I_1^C peaked at 526 nm (E = 2.3574 eV) is usually identified with the line 524.96 nm in the bulk material. The shift of its spectral position is explained in this case by the presence of mechanical stresses, and the position itself is calculated from the shifts of the free-exciton lines. However, a deformation-related shift of I_1^C band does not coincide with the deformation shift of the free-exciton line (see table) and, consequently, the line I_1^C cannot correspond to the line peaked at 524 nm in the bulk material. At the same time, one cannot rule out the presence of doubly charged acceptors (e.g., silicon or carbon, which are the typical residual impurities) in the layers studied. Therefore, the line I_1^C can be a superposition of lines of excitons bound with the doubly charged acceptor and the line of dislocation-related emission. This assumption is supported by a complex structure of this line well-pronounced in Fig. 2 and by an increase in the distance between the components of the line with an increase in strain.

The X-ray diffraction studies we have carried out allow us to suggest the following qualitative model that explains the appearance and nature of the I_1^C line:

Since its intensity increases with an increase in the mosaic size, we may assume that the centers, which caused this band, are related to the defects inside the misoriented blocks, probably with the boundaries of subblocks, which are composed of the mosaic and produce the acceptor levels in the forbidden gap. The transition I_1^C can be related to the radiative recombination of exciton bound with dislocations.

CONCLUSION

It is shown that the change of the MBE growth of the epitaxial buffer ZnTe/GaAs layers (i) by using a thin recrystallized buffer ZnTe layer ($d \sim 10$ nm), as well as (ii) by increasing the buffer layer thickness, results in the improvement of the epilayer structure (a decrease in the rocking curve half-width and an increase in the mosaic sizes), in the enhancement of the total overall intensity of PL bands in the excitonic region of the spectrum, and in a decrease in intensity at longer wavelengths.

We obtained additional information about the nature of I_1^C and on the band found nearby (I_X). The difference between the temperature and strain dependences of the positions of these bands and the corresponding characteristics of the exciton emission lines, as well as the enhancement of their intensity as the strain was decreased, allowed us to relate these bands to extended defects. This conclusion is confirmed by the similarity of their behavior and the behavior of dislocation-related emission bands in II–VI single crystals. It is assumed on the basis of these data and results of X-ray diffraction measurements that the centers responsible for I_1^C band are related to the subblock boundaries in the mosaic structure.

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