Molecular-beam epitaxial growth of CdZnTe/ZnTe QW structures and superlattices on GaAs (100) substrates for optoelectronics

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ABSTRACT

The effect of the 5 nm thick ZnTe intermediate layers obtained by solid phase crystallization at growth temperature on the optical properties of ZnTe epilayers grown by molecular beam epitaxy (MBE) on (100) GaAs substrates has been investigated by low temperature photoluminescence and reflectance spectroscopy. Reduction of nonradiative center concentration and improvement of ZnTe epilayer photoluminescence characteristics have been achieved using of solid phase crystallized intermediate layers. At the same time defect (V_{Zn} and Ga_{Zn}) depth nonuniformity was found to occur in ZnTe epilayers with and without such intermediate layers. Use of such surfactant layer and optimized technology conditions on early stage of growth makes possible to obtain CdZnTe/ZnTe quantum wells and super lattices with high luminescence efficiency for further application.

Keywords: molecular beam epitaxy (MBE), photoluminescence (PL), ZnTe/GaAs, CdZnTe/ZnTe quantum wells, superlattices.

1. INTRODUCTION

In recent years a lot attention has been paid to the single and multilayers ZnTe and CdTe on GaAs heterostructure investigation aimed at realizing highly strained superlattices, SLs, such as ZnTe/ZnS[1], ZnSe/ZnTe[2] and CdTe/ZnTe[3] with ZnTe and CdTe buffer layers for other II-VI compound based devices[4-6].

Molecular beam epitaxy, MBE, is promising technique for the epitaxial growth of high quality ZnTe and CdTe based structures on GaAs for optoelectronic devices[7]. But using of GaAs as a substrate put forward the problems of high lattice mismatch (~7.6% for ZnTe/GaAs) and thermal expansion differences. It causes three dimensional growth (3D) at early stage of epitaxy resulting in the poor quality of the buffer layers.

It is known, that the density of defects in layers strongly depends both on the growth mode of the system and on the mechanism of defect generation during growth processes. The problem in such lattice mismatched heterostructures is to reduce the crystalline defects concentration connected with 3D-growth. It can be solved by using of thin buffer layer (usually amorphous or polycrystalline) which allow to reduce substrate surface energy due to reduction of surface tension forces and provide possibility of layer-by-layer growth. The growth mode is determined not only accomplished by energetics, but also by kinetics of growth. Several methods are used usually for delaying the 2D→3D transition: (i) MBE growth at low temperature; (ii) high growth rate; (iii) use of surfactants or intermediate layers.

In present study we improved the quality of ZnTe buffer layers and grew $Cd_{1-x}Zn_xTe$/ZnTe single and multiquantum wells, QWs, structures and SLs by use of a 50 Å thick ZnTe intermediate layer subjected to solid phase crystallization by heating up to 300-350 °C. The intermediate ZnTe layer effect on structure quality of buffer ZnTe epilayers, ELs, for further optoelectronic application have been investigated by optical and X-ray methods.

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2. TECHNOLOGY AND EXPERIMENTAL METHODS

All structures were grown by MBE on semiinsulating (100) GaAs substrates in a CATUN' machine equipped with conventional effusion cells for high purity elements (99.9999) evaporation. For deoxidation the GaAs substrates were heated up to a temperature ~ 550-580 °C. If we used the process of ZnTe buffer layer growth without intermediate layer (process I) the samples were cooled down to 250-280 °C and after that GaAs surface was exposured to Zn/Te beam with pressure ratio (I_{Zn}/I_{Te}=1:2) that result in *a*(2x1) surface reconstruction, i.e. Te-rich surface. Reflection high-energy electron diffraction (RHEED) was applied for control of the surface during deoxidation and growth process.

During the growth process temperature of the substrate was increased up to $T_G \approx 350$ °C (growth temperature) as well as the Zn/Te beam pressure ratio was changed to provide *a*(2x1) and *c*(2x2) reconstruction for near stoichiometry conditions. The growth of last 10 nm thick epilayer was followed by cooling to have (2x1) reconstructions. Reconstruction become *c*(2x2) after cooling down to room temperature.

For II-type processes (with intermediate layer) the oxide-free GaAs substrate (as for I-type process) was slowly (~10 h) cooled down to room temperature. After cooling the substrate was firstly covered by an amorphous 1 nm thick ZnTe intermediate layer followed by its solid phase crystallization by heating up to growth temperature before epitaxy. The subsequent procedures were as in process I. The ZnTe buffer layers were grown of 1.5 μm thick (process I); 1.5 μm and 2 μm thick (process II).

Three types of structures with QWs and SLs were grown:

(i) The structure consisted of $Cd_{1-x}Zn_xTe$ (x=0.6÷0.8) alloy single well sandwiched between cap and buffer layers of ZnTe which acted as barriers. Samples contain the wells of 50 Å width;

(ii) The structures consisted of three $Cd_{1-x}Zn_xTe$ quantum wells (MQWs) 80 Å, 40 Å and 20 Å wide;

(iii) The $Cd_{0.3}Zn_{0.7}Te$/ZnTe strained superlattices (SLS) consisted of 15 periods with 20 Å equal layer thickness or 10 periods with thickness of $Cd_{0.3}Zn_{0.7}Te$ layer - 50 Å and ZnTe layer - 250 Å.

The growth temperature for $Cd_{1-x}Zn_xTe$ (x=0.6-0.8) compounds was ~300 °C. All structures with QW and SLs had a 400 Å cap ZnTe layer and 1.5 μm thick ZnTe buffer layer with solid phase crystallized ZnTe thin (50-100 Å) layer on GaAs substrate (process II).

The optical investigations (low temperature photoluminescence, PL, and reflectance measurements) have been used to ascertain the quality of structures. PL was excited by Ar^+ laser. X-ray rocking curve measurements performed on a double-crystal diffractometer (Θ and $\Theta/2\Theta$ scan) were carried out too.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The low temperature (≤ 11 K) PL spectra of ZnTe ELs are usually divided into three regions of energy:

(i) free or bound exciton transitions (2.25-2.39 eV; 551-519 nm);

(ii) donor-acceptor pairs (DAP) recombination (2.12-2.25 eV; 590-551 nm);

(iii) PL transitions connected with deep-level defects (1.6-2.1 eV; 775-590 nm).

Let's consider the near band emission firstly. Fig.1 presents the PL spectra of ZnTe ELs of different thicknesses grown with the stage of solid phase crystallization (process I, curves b,c) and without thin intermediate layer (process II, curve a) excited by 0.488 μm - line of Ar^+ laser and measured at 4.2 K in the near band gap region. All the spectra consist of free exciton bands I_{FX} (λ=520.2 and 521.2 nm)[10], excitons bound to donor (probably Ga_{Zn}) I_2 (D^0X) (λ=522.2 nm)[11], and two emission lines of acceptor bound excitons: I_1'(A°X) with (λ=523.4 nm) and I_1^C(A°X) with (λ=526.0-526.24 nm). The I_1' line was attributed to excitons bound to V_{Zn} or As_{Te}[10]. A transition (I_1') commonly observed in bulk ZnTe (sometimes labeled as A_1^C) was associated with a Zn-vacancy complex[10]. The identification of luminescent transitions in such ZnTe ELs was carried out by analysis of their positions and line shape at 4.2 K, by the temperature dependence in the range from 4.2 K to about 80 K of their intensities and by comparison with numerous literature data for ZnTe/GaAs ELs of the same thickness[12,13].

The bound exciton emission lines (D^0X and I_1^C) are dominated. No sizable spectral change was observed in the both type of growth processes. We observed only unessential shift of a D^0X and I_1^C exciton bands to lower energy (~ 2 meV) on ELs without intermediate layer. A similar shift may be caused by higher tensile strain in ZnTe/GaAs layers without intermediate layer in comparison with the ELs grown with such layer. We noted that the overall integral intensity of the near-band emission (free and bound exciton intensity) increases noticeable while the deep level transition (λ=650-700 nm) slightly decreases when the samples are grown by process II. The increase of near-band emission intensity may be attributed to reduction of concentration of nonradiative recombination centers which are probably connected with structural defects. The decrease of deep level transition intensities is the evidence of reduction of corresponding center density. Both facts testify to EL quality improvement.

It should be noted that the heights of I_2 and I_1' peaks normalized to I_{FX} peak intensity are similar in the case of process I and process II. So we pointed out that the intermediate layer doesn't prevent completely the diffusion at the interface.

It is known from transmission electron microscopy data[14] that ZnTe epilayers grown at T_G=300°C (technology conditions are similar to that for process I) on GaAs substrates contains the increased dislocation density and Te precipitates near the surface of the films thicker than about 1 μm. It was expedient to investigate the ZnTe epilayers quality by depth resolved method. We used the PL measurements at various wave length excitaiton as in[15]. We investigated the influence of laser excitation level (from 10^{17} cm^{-2} to 10^{19} cm^{-2}) on the change of ZnTe PL spectra preliminary and obtained no essential change of different peak ratio in near band edge region.

Fig.2 shows low temperature PL spectra for ZnTe layer grown by the process II, measured at different excitatation wavelengths ($\lambda_{1,2,3}$=0.4756, 0.4880 and 0.5145 μm of Ar^+ laser) under low pump level ($P_{exc}<1x10^{18}$ quants/cm^2). The absorption coefficient α in this energy range changes from ~10^4 to 10^5 cm^{-1} approximately[16], so depth penetration of excitation light changes from ≈0.1 to about 1 μm. It is seen that decrease of λ_{exc} (increase of α) results in the decrease of excitation luminescence intensity in general and in the increase of bound (V_{Zn}, Ga_{Zn}) to free exciton intensity ratio. This suggests an increase of donor and acceptor (probably Ga_{Zn} and V_{Zn}) concentration near the surface of the ZnTe epilayer.

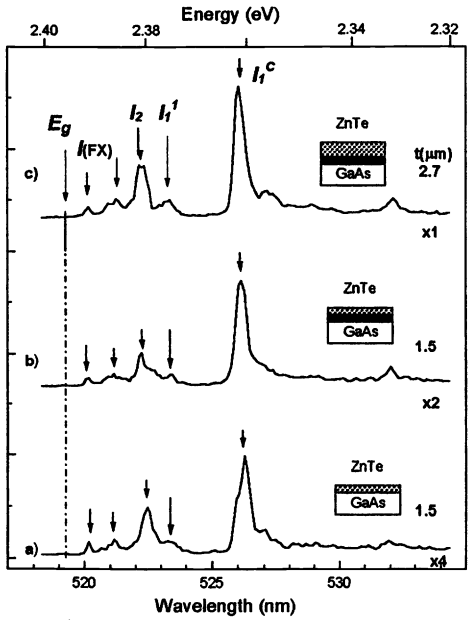

Fig. 1. Photoluminescence spectra at 4.2 K for ZnTe/(001)GaAs epilayers grown on the substrates prepared (a) by process I, and (b,c) by process II. λ_{EXC}=488.0 nm, $P_{EXC}=2\cdot10^{17}$ quants /cm^2·s .

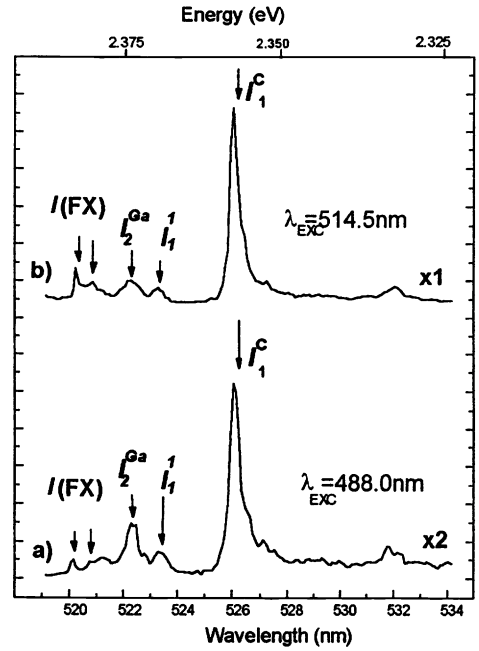

Fig.2. Photoluminescence spectra at 4.2 K for ZnTe/(001)GaAs layer grown in the two-step process, measured at two different excitation wavelengths. $P_{EXC}=2\cdot10^{17}$ quants/cm^2.

So we can conclude that higher defect density takes place in the near top surface region independently on the presence of intermediate layer. Thus thick ZnTe ELs contain two regions with higher point defect concentration: near interface region[7] and near top surface epilayer one. It is known[14] that higher concentration of extended defects are present in these regions also.

For subsequent study of the potentiality employed by MBE technology we grew single, multiquantum wells, structures and SLs with above mentioned parameters. X-ray diffraction, XRD, measurements were also made on CdZnTe/ZnTe SLs. Superlattice satellits of (±2) order were present in XRD rocking curves (Θ /2Θ scan) that is the evidence to regular periodicity of structure. Fig.3 demonstrate a good quality of $Cd_{1-x}Zn_xTe$/ZnTe SLs grown with optimization of the early stage of epitaxy (process II) that manifest itself in effective emission about order more intensive than from ZnTe ELs with full width at half maximum, FWHM, ~ 9 meV at 4.2 K. Fig.4 shows photoluminescence spectra at 4.2 K (a) and 77 K (b) of the sample with three single $Cd_{1-x}Zn_xTe$ quantum wells of different thickness separated by a 30 nm thick ZnTe barriers. The PL spectra of the QWs show a strong lines from the heavy-hole free excitons for each well. These lines (FWHM ~ 9-16 meV at 4.2 K) are much stronger than excitonic PL from thick CdZnTe/GaAs ELs.

As can be seen from Fig.3 and Fig.4 strong PL was observed both at 4.2 and at 77 K which is an indication of high ZnTe and $Cd_{1-x}Zn_xTe$ material quality.

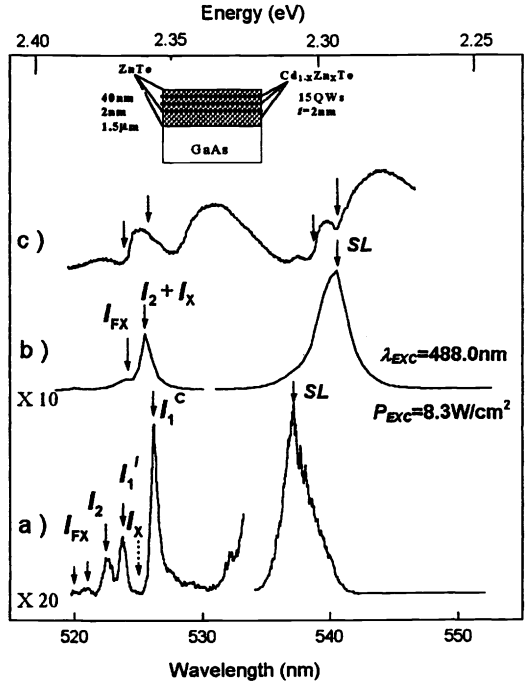

Fig. 3. Photoluminescence (a,b) and reflection (c) spectra at 77 K and PL spectrum at 4.2 K (a) and 77 K (b,c) for ZnCdTe-ZnTe/(001)GaAs SLs. $P_{EXC}=2\cdot10^{17}$ quants /cm^2•s.

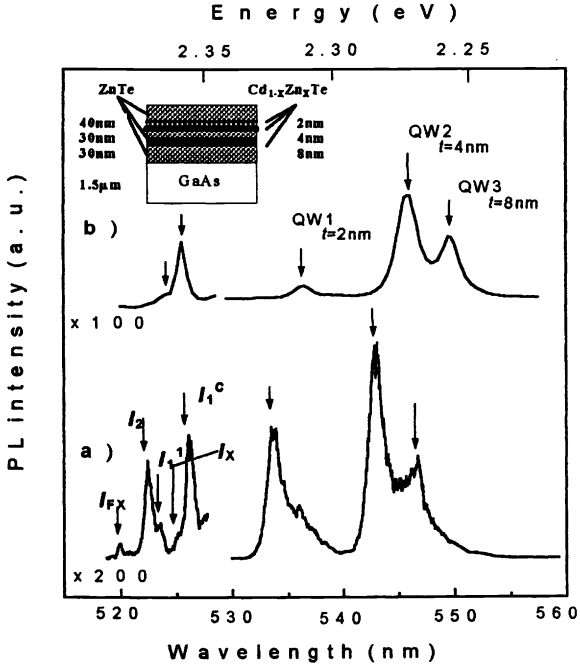

Fig. 4. Photoluminescence spectra at 4.2 K (a) and 77 K (b) of the sample with three single $Cd_{1-X}Zn_XTe$ quantum wells separated by a 30 nm thick ZnTe barriers. λ_{EXC}=488.0nm. $P_{EXC}=2\cdot10^{17}$ quants/cm^2•s.

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