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Lateral and depth inhomogeneities in Zn-based heterostructures grown on GaAs by MBE

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The near-surface morphology, crystalline quality and contamination as well as depth and lateral homogeneity of background impurities and defects distribution in undoped ZnSe and ZnTe films grown by molecular beam epitaxy on GaAs(001) substrates were studied. The improvement of structural quality with the increase of film thickness was observed by X-ray diffraction and atomic force microscope. But sufficient depth inhomogeneity of point and extended defect distribution is present in all films independently on their thickness and increases after deposition of quantum wells. Transversal photovoltage measurements confirm the laminar inhomogeneity of investigated films. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Molecular beam epitaxy; Zn-based heterostructures; ZnSe films; ZnTe films; Atomic force microscopy; X-ray diffraction

1. Introduction

Zn-based II–VI semiconductor multilayer heterostructures are of great interest for the fabrication of optoelectronic devices (light emitting diodes, lasers, photodetectors, solar cells, etc. [1–3]). Molecular beam epitaxy (MBE) is a convenient technique for the epitaxial growth of ZnSe and ZnTe based structures on GaAs. But using of GaAs as a substrate put forward the problems of high lattice mismatch (~ 7.6% for ZnTe/GaAs) and thermal expansion factor differences. It can leads to three dimensional growth (3D) at early stage of epitaxy as well as to lateral and depth inhomogeneity of epilayers which results in poor quality of epilayers and can accelerate the degradation processes. So, control of point and extended defect distribution is important.

We present a study of the in-plane and out-of plane inhomogeneity of the properties of ZnSe and ZnTe films obtained under various technology conditions. The influence of epilayer thickness and quantum size layer deposition on such inhomogeneity has been investigated. X-ray and optical methods, as well as transverse voltage technique [4] and atomic force microscopy, AFM, have been used for investigation.

2. Experimental details

All nominally undoped ZnSe and ZnTe films of different thickness (0.5–5.7 μm) and structures with quantum size layers were grown by MBE method on semi-insulating GaAs(001) substrates in a CATUN' machine equipped with conventional effusion cells for high purity elements. The residual pressure in the chamber was $\sim 8 \times 10^{-11}$ 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 diffraction, RHEED, was applied to control the surface during deoxidation and deposition processes. Before the deposition of ZnSe epilayer.

GaAs surface was treated in Zn flux during 100 s at pressure $\sim 4 \times 10^{-7}$ Torr for prevention the chemical reaction of Se and the excess Ga on the GaAs surface. For ZnTe films growth the intermediate (surfactant) ZnTe layer between GaAs and ZnTe film was used as a rule. In this case 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 films of 1.5–5.7 μm thickness. The growth temperatures were 260–340°C for ZnSe, 350°C for ZnTe, and 300°C for $Cd_{0.3}Zn_{0.7}Te$ quantum size layers, Zn/Te or Se/Zn beam pressure ratios were $I_{Zn}/I_{Te} = 1:2$ and $I_{Se}/I_{Zn} = 1.2–1.5$

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Table 1
Technology conditions and initial of ZnSe films (*, high resistivity)

Sample, N	Technology conditions			Epitaxial film parameters			
	Se/Zn ratio	T_G (°C)	Surface reconstruction	Thickness (μm)	$n_{300\,K}$ (cm^{-1})	Mobility, $\mu_{300\,K}$ ($cm^2/V\,s$)	Zn or Se rich surface
50	1.2	300	$c(2\times2)$	2.0	*	*	Zn
11	1.2	300	$c(2\times2)$	1.3	*	*	Zn
34	1.2	300	$c(2\times2)$	0.5	8×10^{17}	220	Zn
35	1.2	260	$c(2\times1)$	0.5	1.3×10^{18}	190	Se

for ZnTe and ZnSe, respectively. Typical growth rate was ~ 0.6 μm/h. The free carrier concentration, n, and mobility, μ, for ZnSe films were obtained from Hall effect measurements at 300 K. Some parameters of growth process of investigated ZnSe and ZnTe films are listed in Tables 1 and 2, respectively.

We used X-ray diffraction method as well as AFM for film structural quality and morphology characterization. Depth resolved low temperature photoluminescence and transversal photo-emf method were applied for control of film depth and lateral inhomogeneity. AFM investigation was performed with Scanning Probe Nanoscope IIIa in tapping mode. Silicium nitride tipe size was 10 nm. Photoluminescence 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 spectra were recorded in the range from 440 to 550 nm at 4.2 K using the grating spectrometer MDR-23. Depth inhomogeneity of ZnSe and ZnTe films were investigated with step etching in special solution which contained Br_2, HCl and dioxane. Depth distribution of radiative centres in ZnTe films was investigated by PL method using the excitation by the light of different wavelengths [5] that correspond to different absorption coefficients ($\alpha \approx 10^4$–10^5 cm^{-1} for $\lambda \approx$ 0.476–0.514 nm) [6,7]. Excitation light intensity was chosen in such a way to equalize excitation levels at different wavelengths.

The transversal photovoltage was exited simultaneously with modulated and non-modulated light beam of different wavelength that allow to determine the depth and lateral distribution of 'drift' and 'recombination' energy barriers connected with inhomogeneous distribution of defects and impurities in MBE-films.

3. Results and discussion

X-ray diffraction method was used for study of structural quality dependence on epilayer thickness and surfactant layer deposition. The (004) rocking curves for a ZnTe films of different thickness are shown on Fig. 1. The full width at half maximum, FWHM, of X-ray rocking curves decreased monotonically with film thickness (see Table 2). However, the value of FWHM obtained for the most thick (5.7 μm) film was about 90 arcsec that exceeds the value for a bulk material. Deposition of surfactant layer led to decrease of FWHM too.

It should be noted that the high value of FWHM of ZnTe films is attributed often to their mosaic structure [8,9]. Under this assumption the decrease of rocking curve line width with the increase of film thickness can be explained by the increase of size of crystalline mosaic blocks or diminishing of their disorientation.

For ZnSe films effect of FWHM decrease with film thickness increase over 0.5 μm was observed also. It is apparently connected with exceeding of film thickness over the thickness of defect interface region where misfit dislocations are localized mainly [10].

The surface morphology of MBE deposited ZnTe-based films were examined by AFM. A typical images of a part of growth region for ZnTe films of different thickness (Nos. 88 and 147, Table 2) are shown on Fig. 2. It is seen that surface of investigated films consists of islands of different size but surface morphology of thin (Fig. 2a) and thick (Fig. 2b) films are different. Roughness of the last one is smaller and island arrangement become more regular.

Both AFM and X-ray diffraction methods testify to the

Table 2
Initial parameters of ZnSe films

Sample, N	Epitaxial film thickness (μm)	Intermediate ZnTe layer, 5 nm	Quantum wells	Cap ZnTe layer, 40 nm	FWHM (arcsec)
147	5.7	+	–	–	~ 90
144	3	+	–	–	~ 127
67	2.7	+	–	–	~ 312
90	1.5	+	–	–	~ 360
88	1.5	–	–	–	~ 560
114	1.5	+	3 QWs $Cd_{0.3}Zn_{0.7}Te$ $L_1 = L_2 = L_3 = 2$ nm, $L_B = 30$ nm	+	–

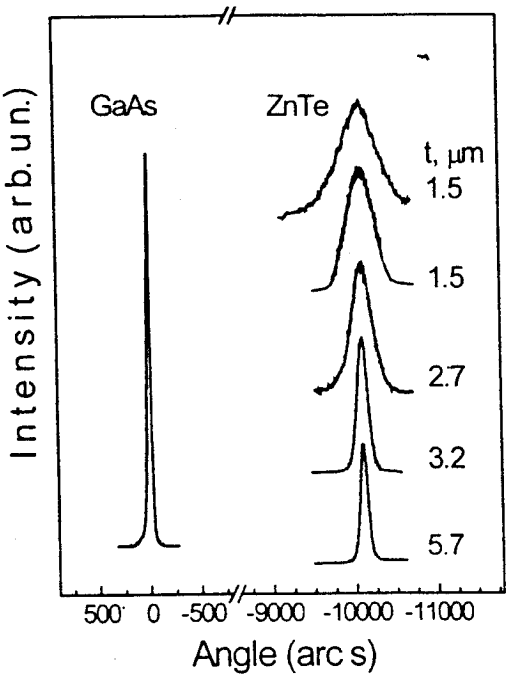

Fig. 1. X-ray double-crystal rocking curves [(004)reflection,CuK$_{\alpha 1}$radiation] for ZnTe films of different thickness. The top trace was obtained from a 1.5 μm film (No. 88) and has a FWHM of ~ 500 arcsec. The lowest trace was obtained from a 5.7 μm film (No. 147) and has a FWHM of ~ 90 arcsec. The GaAs substrate (FWHM = 36 arcsec) is shown for comparison. The curves have been arbitrarily shifted along axis.

improvement of ZnTe film crystalline quality with the increase of its thickness up to 5.7 μm.

The depth distribution of extended and point defects in ZnTe films was controlled by the dependence of excitonic photoluminescence line intensity on excitation wavelengths that corresponds to different light penetration depth. Such dependencies of donor (acceptor) bound exciton peak intensity I_2^{Ga} (I_1') and line intensity of exciton bound to V_{Zn}/dislocation complexes I_1^C [11], normalized to free exciton line one, I_{FX}, are shown on Fig. 3. Depth distribution of I_2^{Ga}/I_{FX}, I_1'/I_{FX}, and I_1^C/I_{FX} values for the films with various thickness, as well as for the films with quantum wells reveals the depth dependence of defect concentration to be non-uniform: donor, acceptor and extended defect concentration increases towards the surface of the films.

The similar dependencies obtained with step by step etching were observed for ZnSe films also [12].

Fig. 4 presents a distribution of the transverse photovoltage as monochromatic narrow light probe (monochromatic modulated light beam) is moved along the sample from one contact to another. Curve (3) corresponds to light wavelength $\lambda_{exc} = 0.44$ μm ($E = 2.82$ eV), while curves (2) and (3) is obtained under $\lambda_{exc} = 0.88$ μm ($E = 1.40$ eV) excitation. Curves (1) and (2) were measured at the intensity of modulated exciting light $G = 2 \times 10^{12}$ cm^{-2} s^{-1} and curve (3) at $G = 2 \times 10^{14}$ cm^{-2} s^{-1}. It can be seen from Fig. 4 that distribution of photovoltage at $\lambda_{exc} = 0.44$ and 0.88 μm is nearly the same, but the increase of the intensity of the exciting light results in inversion of the photovoltage distribution [curves(2)and(3)].

The experimental data for Fig. 4 were obtained by use of synchronous detection method. In this method a certain amplitude and phase corresponds to 'effective' lifetime (τ_{ef}) of electron–hole pairs: $\tau_{ef} = \tau_0 \exp(\vartheta)$, where τ_0 is the life time of the electron–hole pairs, when recombination barriers are absent, $\vartheta = E_{rec}/(kT)$; where E_{rec} is the height of the barrier, k is the Boltzmann constant and T is the temperature. Such amplitude and phase change is an evidence of the lifetime change. It may be determined by the height of recombination-drift barriers alteration. In another words, it indicates the depth non-uniformity of the heterostructures ZnSe/GaAs properties (τ_{ef} and $d\rho/dx$), its 'lamination'.

The difference between the spectral characteristics of the transverse photovoltage obtained by scanning of the excitation wavelength from $\lambda_1 = 0.4$ μm to $\lambda_n = 0.92$ μm and in opposite direction from λ_n to λ_1 which depends on the velocity of wavelength scanning was revealed. This is due

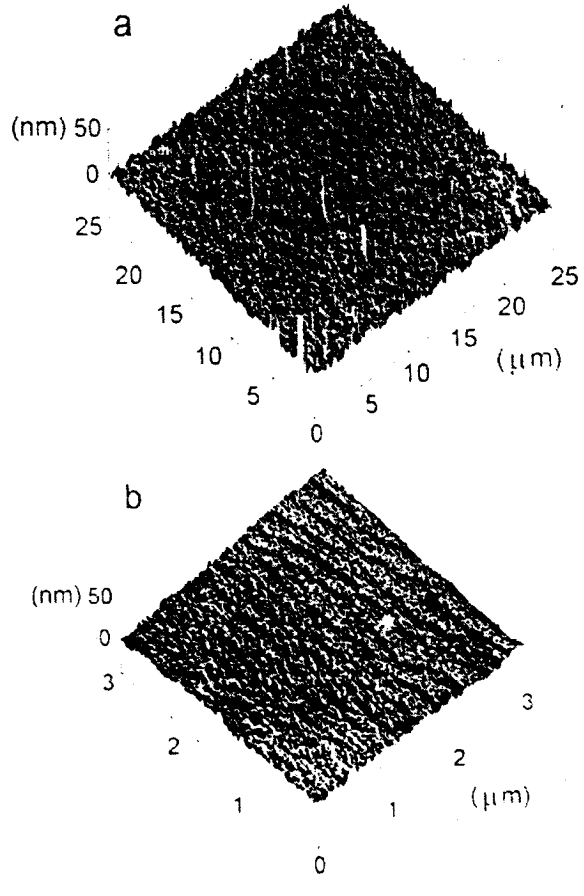

Fig. 2. AFM images for surface of ZnTe films grown by MBE at 380°C directly on a GaAs(001) substrate (a) and ZnTe films grown on a GaAs(001) substrate using solid phase crystallization of thin amorphous ZnTe intermediate layer (b). Thickness of ZnTe film is about 1.5 (a) and 5.7 μm (b).

to persistent photovoltage connected with a system of 'drift' an 'recombination' barriers which are distributed in depth of ZnSe films and confirms the 'lamination' of investigated films.

We suppose that depth distribution of defects in II–VI films grown by MBE on GaAs substrates are conditioned by growth mechanism, interface reactions and interdiffusion of components. In addition their inhomogeneity may be connected with the presence of native mobile defects that is the specific feature of II–VI materials.

4. Conclusion

X-ray diffraction and AFM study of crystalline quality and near-surface morphology of undoped ZnSe and ZnTe films grown by molecular beam epitaxy on GaAs(001) substrate has shown the improvement of structural quality with the increase of film thickness. Deposition of thin (~ 5 nm) intermediate solid phase crystallized amorphous ZnTe layer has been found to result in the same effect. The use of depth resolved PL method revealed the sufficient depth inhomogeneity of radiative point and extended defect distribution in ZnSe and ZnTe films independently on their thickness, which increased after quantum well deposition. This laminar inhomogeneity was confirmed by transversal photovoltage measurements of the investigated films.

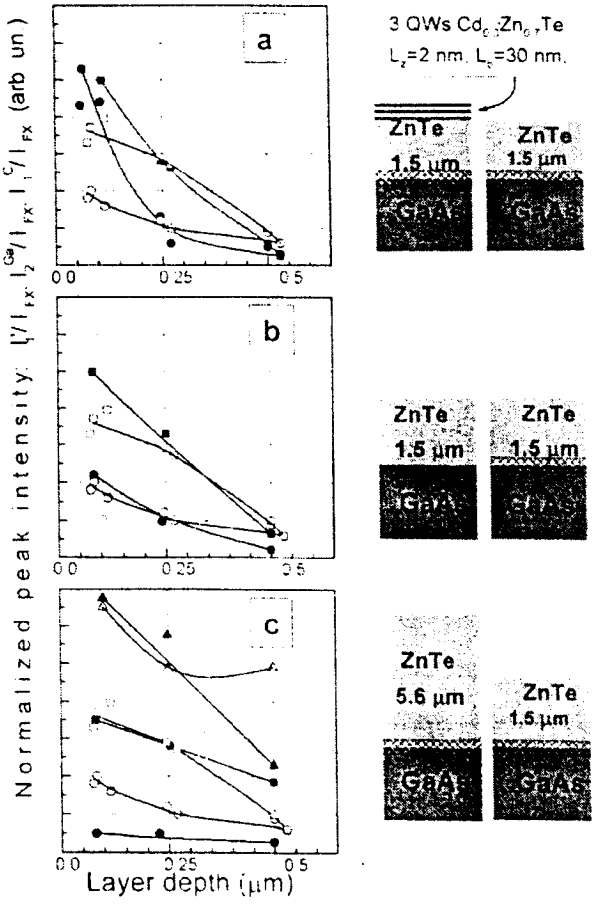

Fig. 3. Depth distribution of ratios I_2^{Ga}/I_{FX} (□), (■), I_1'/I_{FX} (○), (●) and I_1^C/I_{FX} (△), (▲) in the: (a) ZnTe films of 1.5 μm thickness (No. 90) open signs and 1.5 μm thickness with three quantum well deposition (No. 104) solid signs; (b) ZnTe films of 1.5 μm thickness (No. 90) open signs and 1.5 μm thickness (No. 88) solid signs; (c) ZnTe films of 1.5 μm thickness (No. 90) open signs and 5.7 μm thickness (No. 147) solid signs.

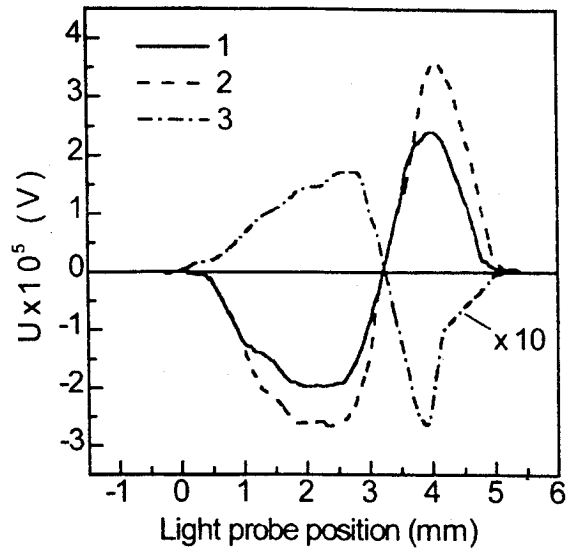

Fig. 4. Transverse photovoltage distribution in ZnSe/GaAs heteroepitaxial film (No. 50) at scanning along the sample with different excitation level of modulated illumination: 1.2–2 × 10^{14} and 3–2 × 10^{14} cm^{-2} s^{-1} for different excitation wavelengths (1–0.44 and 2.3–0.88 μm).

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