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RAMAN AND PHOTOLUMINESCENCE SPECTROSCOPY OF LOWTEMPERATURE HETEROSTRUCTURES AlGaAs/GaAs(100)

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Abstract. Methods of Raman backscattering and photoluminescence spectroscopy allowed to study substructure and luminescence of epitaxial low temperature MOCVD AlGaAs/GaAs (100) heterostructures. It is shown, that experimental data received during work correlate with results of the structural and optical researches accomplished in the previous work. The assumption that at high concentration of a carbon acceptor atoms concentrate on defects of a crystal lattice of AlGaAs solid solution with formation of carbon nanoclusters is confirmed.

Keywords: Raman backscattering, photoluminescence spectroscopy, low temperature heterostructures AlGaAs.

INTRODUCTION

Epitaxial films and heterostructures on the basis of A^3B^5 semi-conductor solid solutions are of a great interest in the electronic industry, including solar power [1, 2]. Throughout many years they are to be objects of intensive researches by various methods. However, the greatest attention is now given to investigations of essentially new properties revealing at growth of epitaxial films with quantum-dimensional inhomogeneity, and also at reception of compounds in these systems using new methods [3, 4].

Thus in our previous work [5] it was shown, that epitaxial films of AlGaAs solid solutions which has been grown up by MOCVD method at lowered temperature and minimum parity of 5 and 3 groups elements, as well as disordered substitutional solid solutions, had crystal sphalerite structure. However, parameters of their crystal lattices were less than GaAs substrate lattice parameter, i.e. the full mismatch with Vegrd's law from [6] was observed. To explain this fact it was necessary to admit, that atoms of gallium in metal sublattice when formating solid solution are not replaced with atoms of aluminums, and the released places remain vacant. But for this purpose vacancies should be formed only in the centres of facet of sphalerite lattices since only under such condition the parameter of a crystal lattice can be less than GaAs parameter. Hence, when concentration of atoms of aluminums is in range of $0 < x < 1$ at lowered temperature technologies of growth the formation of a solid solution of subtraction AlGaAs originates.

However, reduction of lattice parameters for GaAs and AlGaAs at greater concentrations of acceptor impurity (carbon) may happen as a result of carbon embedding in metal sublattice [4, 7]. Compression of a crystal lattice in this case will have though not such a big value as at formation of solid solutions of subtraction, but at a stage of film growth, undoubtedly, it will lead to creation of solid solution substructure and a possible congestion of carbon in places of defects of a lattice, that should be reflected in material power characteristic, such as width of energy band-gap. Therefore in the given investigation for studying of structural features of low temperature AlGaAs films formation with high concentration of carbon acceptor impurity the Raman spectroscopy has been used. As oscillatory spectra of a lattice of various layers are observed as combination of spectrum of each layer, using this tool we have possibility to study separate layers, not hurting structure with various laser lines of excitation with various depths of penetration. And secondly, bearing in mind that lattice fluctuations are very sensitive to the nearest atoms — we can investigate crystal structure and its quality in extremely small scale: in range of lattice parameter, and consequently use of Raman dispersion gives additional, new and sometimes more detailed information concerning properties and qualities of thin films.

Attraction of Photoluminescence spectroscopy as a method of studying of the energy band-gap width changing, as a concentration function of carbon acceptor impurity was also used.

Thus, the main purpose of our investigations at this step was studying of lowtemperature AlGaAs epitaxial solid solution substructures, and also influence of high concentration of carbon on energy spectra.

OBJECTS AND RESEARCH METHODS

Samples of AlGaAs/GaAs (100) heterostructures have been grown up with a research objective of autodoping processes for achievement of the maximum concentration of a carbon acceptor. Experiments were carried out for this purpose at the lowered temperature and minimum (2—3) parity of 5 and 3 groups of elements depending on set structure of a solid solution.

Samples EM1540, EM1555, EM1585 have been received on installation of MOCVD «EMCORE GS 3/100» in a vertical reactor with high speed of rotation of lattice holder. The temperature of lattice holder was kept up the 550° C, 77 Torr pressure in a reactor, 1000 rpm speed of rotation of lattice holder. As initial reagents were used $Ga(CH_3)_3$, $Al(CH_3)_3$ and AsH_3. The thickness and structure of grown up layers have been defined with use of scanning electronic microscopy and the dispersive analysis. For comparison of properties of samples received by a new technique and normal technology EM1017 sample, grown up under normal conditions, was used.

Structures, crystal lattice parameters and thickness of samples are resulted in Table 1.

Raman dispersion spectra received using Raman microscope SENTERRA Bruker with lines of excitation 532 nm and capacity of laser radiation 20 mW.

Photoluminescence spectra have been received at a room temperature on spectrometer Horiba Jobin HR800 with excitation on 633 nanometers.

Table 1. Composition and film thickness for heterostructures AlGaAs/GaAs(100)

Sample	Composition	film thickness *d*, μm
EM1017	0.51	~1.0
EM1540	0.00	~1.2
EM1555	0.47(8)	~2.0
EM1585	0.43(8)	~1.5

RESULTS OF RESEARCHES AND THEIR DISCUSSION

RAMAN DISPERSION

Depth of penetration of laser radiation with length of a wave $\lambda = 532$ nanometers and also effective depth of the analysis at Raman dispersion can be defined from a relation $\lambda / 2\pi k$, where k — extinction factor. Accordingly in case of AlAs — GaAs system analysis such depth will be approximately 400 nanometers. It grants a right to say that using the given length of a wave of the laser for Raman dispersion we will receive the information only from lowtemperature layer.

According to rules of selection, received from the Raman dispersion tensor analysis [8] for crystals with diamond structure at backscatter dispersion from (100) surfaces can be observed only LO phonons, and occurrences of TO phonons is forbidden.

On pictures 1, *a* — 1, *d* spectra of Raman dispersion in geometry $x(y,z)x$ — for analyzed samples are presented.

Apparently from picture 1, *a* the Raman spectrum of EM1017 sample received at standard technology contains GaAs and AlAs longitudinal optical phonon modes in a point (Γ), localized nearby ~267 cm^{-1} and ~380 cm^{-1} respectively. The mode of fluctuations with frequency of ~195 cm^{-1} can be correlated with occurrence in AlGaAs solid solution of longitudinal acoustic phonon LA localized in a point (L) of Brillouin zone. Experimental data concerned frequencies of longitudinal optical modes of the normal sample precisely correlate with literary experimental and calculated data [9, 10].

Spectrum of Raman dispersion of GaAs/GaAs (100) (sample EM1540) low temperature homoepitaxial structures contains only longitudinal optical phonons LO (Γ) localized ~293 cm^{-1} (fig. 1, *b*). The received experimental data including the spectrum form for low temperature homoepitaxial sample testifies about non-dislocation the mechanism of such type of growth and excellent structural quality of a film.

Raman spectra of low temperature EM1555 and EM1585 heterostructures resulted in figures 1, *c* — 1, *d*. They contain the same modes as heterostructure EM1017 which has been grown up by method MOCVD under standard conditions: longitudinal optical phonon modes AlAs LO (Γ) and GaAs LO (Γ) and longitudinal acoustic phonon LA (L). Frequencies of active phonon modes for sample EM1555 are the following: $\omega_{\mathrm{GaAs\,LO\,()}}$ ~250 cm^{-1}, $\omega_{\mathrm{AlAs\,LO\,(\Gamma)}}$ ~351 cm^{-1}, $\omega_{\mathrm{LA\,(L)}}$ ~ 192 cm^{-1}, and for sample EM1585: $\omega_{\mathrm{GaAs\,LO\,(\Gamma)}}$ ~253.5 cm^{-1}, $\omega_{\mathrm{AlAs\,LO\,(\Gamma)}}$ ~348.5 cm^{-1}, $\omega_{\mathrm{LA\,(L)}}$ ~ 192.5 cm^{-1}. Comparison of ex-

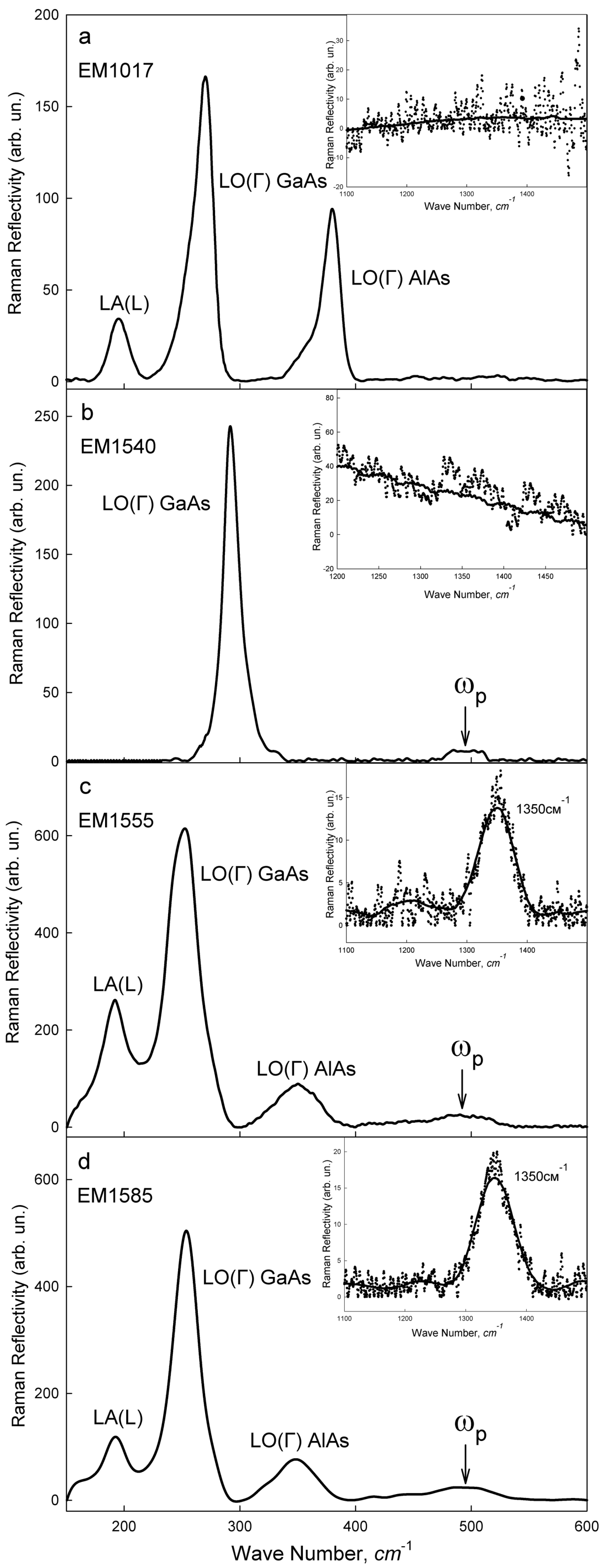

Fig. 1. Raman backscattering for epitaxial heterostructures AlGaAs/GaAs(100): *a* — sample EM1017; *b* — sample EM1540; *c* — sample EM1555; *d* — sample EM1585.

perimental results concerning frequencies of active Raman fluctuations for AlGaAs low temperature solid solutions and similar data for AlGaAs films received on standard technology [9, 10] shows an appreciable difference in sizes of frequencies for homomorphous structures of solid solutions. This consequence of crystal lattice parameter reduction at epitaxial film which has been grown up at the lowered temperature [5] follows from the results of our previous work. The received experimental results about longitudinal optical phonon LO (Γ) frequencies correlate with results of IR-spectroscopy in our previous investigation [5]. Occurrence of modes in area ω_p~500 cm^{-1}, presenting at spectra of low temperature EM1555 and EM1585 samples is connected with occurrence of plasma fluctuations acceptor impurity.

Besides, as it is seen from figures 1, *c* — 1, *d* for low temperature samples the dissymmetric forms of lines for AlAs LO (Γ) and GaAs LO (Γ) active optical phonons are representative, that also is comparable to the given data received by x-ray diffraction method at the previous stage of researches and testifies the deficiency of structure, i.e. about formation of vacancies in a crystal lattice.

It is important to notice, that presence of LA (X) longitudinal acoustic phonons in AlGaAs films received both by a standard technique and by low temperature technology cannot be explained from the point of view of the classical theory of Raman dispersion from a plane (100). Their emergence in the Raman spectrum can be explained by occurrence of structural disorder which appears at replacement of gallium atoms in metal sublattice by atoms of aluminum, especially in near-surface layers as a result of arsenic reverse diffusion [10].

For more information about influence of carbon acceptors on structure defects formation Raman dispersion spectra have been received in the range of 1000—1600 cm^{-1}. Results of these researches are resulted on inserts of figures 1, *a* — 1, *d*. Points designate experimental data, and a continuous line — the simulated average spectrum. As it is seen from graphs, only EM1555 and EM1585 low temperature samples in the range of 1000—1600 contain oscillatory modes. Frequencies of additional active fluctuations are resulted in Table 2. Occurrence of a mode with frequency ~1350 cm^{-1}, attending in low temperature samples spectra, can be explained by occurrence in AlGaAs films of nanocrystalline graphite phase [11—13] arising most likely in places of defects of a crystal lattice. Concerning homoepitaxial low temperature heterostructures, following from the experiment, additional

Table 2. Raman scattering active mode frequencies for AlGaAs/GaAs(100)

Sample	GaAs $\omega_{LO(\Gamma)}$, cm^{-1}	AlAs $\omega_{LO(\Gamma)}$, cm^{-1}	$\omega_{LA(L)}$, cm^{-1}	ω_p, cm^{-1}	Addition modes, cm^{-1}
EM1017	267	380	195	—	—
EM1540	293	—	—	480	—
EM1555	250	351	192	500	1355
EM1585	253,5	348,5	192,5	500	1355

Table 3. Photoluminescence emission energy for heterostructuresAlGaAs/GaAs(100)

Sample	GaAs, eV	AlGaAs, eV	Addition emission energy, eV			
EM1017	1.44	2.03	—	—	—	—
EM1540	1.43	—	—	—	—	—
EM1555	1.45	2.08	—	1.57	1.69	—
EM1585	1.44	2.05	1.38	1.55	1.68	2.31

active modes do not arise. That confirms X-Ray data analysis about structural quality of the sample. However it is necessary to note luminescence occurrence in high-frequency area for homoepitaxial the sample.

PHOTOLUMINESCENCE

Spectra of a photoluminescence from the samples investigated in this work, presented at figures 2, *a* — 2, *d*, have been received at a room temperature in 500—1000 nm area.

Figure 2,*a* shows typical for system GaAs — AlAs spectrum of a photoluminescence of EM1017 sample which has been grown up using standard technology. Here there is a narrow emission line from AlGaAs solid solution and GaAs substrate that was not absorbed by epitaxial layer. Defined energy of emission peaks are resulted in Table 3.

Spectrum of low temperature homoepitaxial GaAs/GaAs (100) structures (sample EM1540), as one would expect, contains one sharp peak with energy ~1.43 eV, being the sum of emissions from a substrate and epitaxial layer (fig. 2, *b*).

And spectra of lowtemperature EM1555 and EM1585 samples (fig. 2, *c* — 2, *d*) have difficult structure which represents two wide emission bands with a number of prominent features in a kind of arm. Decomposition to components of experimental spectra of a photoluminescence lowtemperature EM1555 and EM1585 samples were performed with use of a program complex “New profile 34”. During decomposition it was considered that substrates GaAs (fig. 2, *c* — 2 see, *d*) has to be preliminary simulated and excluded from an overall picture of emission spectra of a photoluminescence. During the modeling process position and semiwidth of experimental peaks were considered.

As it follows from calculated data, the spectrum of $Al_{0.48}Ga_{0.52}As$/GaAs (100) (sample EM1555) low-temperature heterostructures consists of emissions from AlGaAs solid solution and GaAs substrate, corresponding to transitions a zone-to-zone, and also two peaks shifted concerning emissions of a substrate in high-energy area. Results of modeling are presented in Table 3.

As for $Al_{0.43}Ga_{0.57}As$/GaAs (100) heterostructure decomposition of a spectrum of this sample on components has shown, that besides the emission peaks which are responsible for band-to-band transitions in $Al_{0.43}Ga_{0.57}As$ solid solution and GaAs substrate, there are the additional bands shifted to high-energy area concerning emission of a solid solution and a substrate, and also one more peak displaced in the low-energy area concerning emission of GaAs.

It is known, that carbon acceptor recombination bands in spectra of a photoluminescence for GaAs and solid solutions AlGaAs are displaced concerning the basic emission bands in the low-energy side [11, 14, 15]. Such result is observed distinctly only in a spectrum for sample EM1585 where is present displaced rather GaAs peak which, most likely, can appear under condition of occurrence of an impurity from epitaxial layer diffusion. As for emission bands from a solid solution

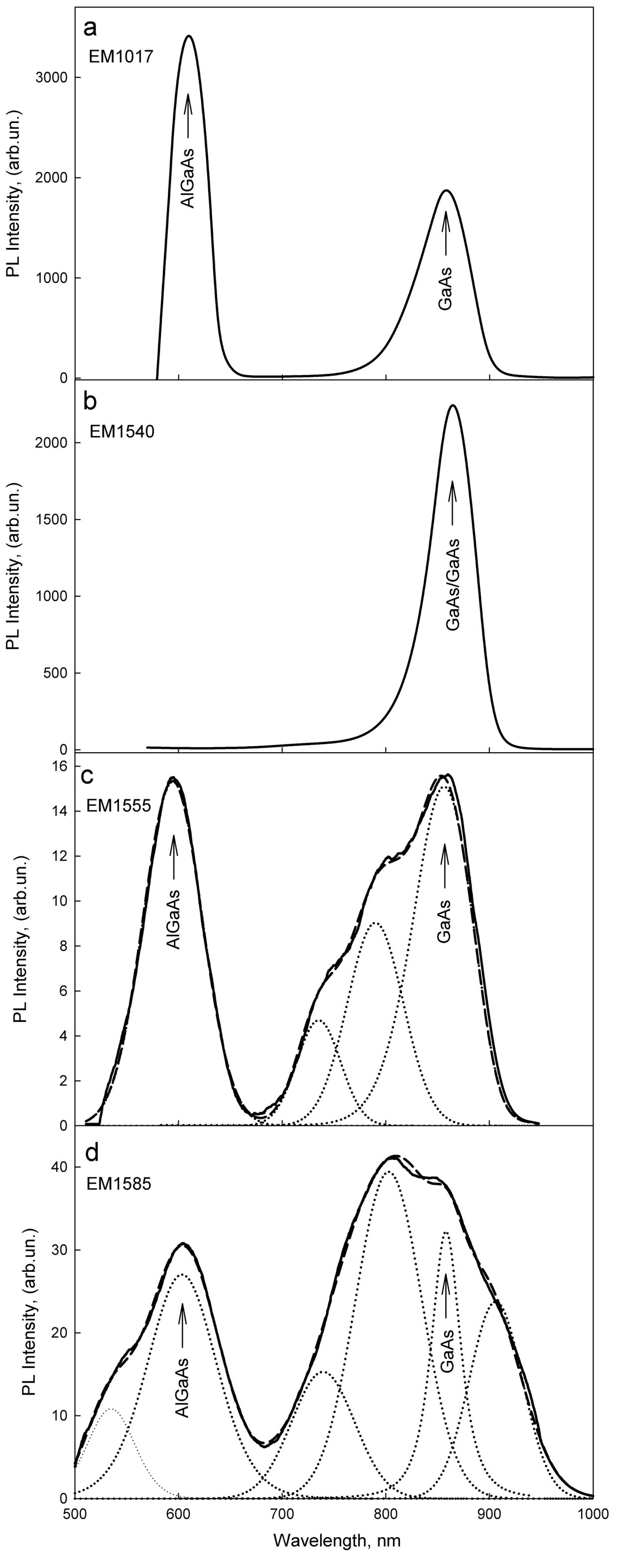

Fig. 2. Experimental and calculation photoluminescence spectra for heterostructures AlGaAs/GaAs(100): *a* — sample EM1017; *b* — sample EM1540; *c* — sample EM1555; *d* — sample EM1585.

for both lowtemperature samples these peaks have considerably greater halfwidth, in comparison with halfwidth of peak of a photoluminescence of AlGaAs solid solution from standard EM1017 heterostructure. This fact can testify the occurrence of acceptor recombination bands slightly displaced relatively a zone-to-zone emission at low concentration of acceptors.

At the same time, on the assumption of experimental and calculated results, in spectra of low temperature EM1555 and EM1585 heterostructures there are two identical emission peaks at intervals 1.55—1.57 eV and 1.68—1.69 eV (see Table 3) which energy maximum grows with rise of concentration of aluminums atoms. Besides, spectrum of a photoluminescence of EM1585 heterostructure encloses one more emission peak with energy 2.31 eV.

Occurrence of the additional emission bands displaced to high-energy area in photoluminescence spectra of low temperature heterostructures is caused in our opinion by formation of carbon nanoclusters, concentrating on defects of a crystal lattice that has been confirmed by a method of Raman spectroscopy.

However it is necessary to notice, that if occurrence of additional high-energy emission near the basic band of low temperature AlGaAs solid solution and connected with carbon nanoclusters is proved by growth of subtraction solid solution, which in itself is defective already, occurrence of similar emission bands near to a luminescence of GaAs substrate at first sight can seem to be unreasonable. More to this, nothing similar was not observed in a spectrum of homoepitaxial low temperature heterostructures. But if to consider, that the crystal lattice parameter of low temperature solid solution is much less than parameter of monocrystal GaAs, used as a substrate, as a result of the occurrence of internal stresses in GaAs near-surface layer carbon diffusion at the initial stage of growth towards a substrate enriches it with carbon which can be accumulated on defects.

CONCLUSIONS

1. By methods of Raman dispersion and Photoluminescence spectroscopy it was shown that gained during the investigation experimental and calculated data correlate with results of the structural and optical researches performed in our previous work [5].

2. Proceeding from results of Raman spectroscopy it is shown that at high concentration of a carbon acceptor atoms concentrate on defects of a crystal lattice of AlGaAs solid solution with formation of carbon nanoclusters.

3. At photoluminescence spectra low temperature epitaxial heterostructures besides band-to-band and

acceptor recombination spectra there are emissive maxima shifted in high-energy area concerning solid solution and a substrate which occurrence is presumably connected with formation of carbon nanoclusters.

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