Quinary InAlGaPAs/GaAs solid solutions grown by temperature gradient zone melting

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Abstract. In this paper we present the results of calculating lattice constant and bandgap InₓAlᵧGa₁₋ₓ₋ᵧPₑ₁₋ₓ₋ₓ₋ₑ₀/GaAs heterostructures at room temperature. The features of growing InAlGaPAs/GaAs quinary solid solution by the temperature gradient zone melting are discussed.

1. Introduction
Using a quinary solid solutions of AIIIBV compounds enable to independently modify the lattice constant, the bandgap and the coefficient of thermal expansion (CTE) [1]. This create opportunities for obtaining isoparametric (izoperiodic and CTE matched) heterostructures based on the binary compounds and working in a wider spectral range than quaternary solid solution [2]. These opportunities open up fundamentally new perspectives for the creation of optoelectronic devices and instruments[3-5]. For use in optoelectronics, such heterostructures must meet high requirements for their crystal structure [6, 7].

One of the available methods for obtaining heterostructures continues to be epitaxy from the liquid phase (LPE) [8]. Despite a number of advantages of the LPE method [9], growing by this method of multicomponent heterostructures of AIIIBV compounds with a controlled composition is difficult due to a temperature change in the growth process. The method of temperature gradient zone melting (TGZM) is economical, since it does not require a large number of initial materials due to small thicknesses of the zones and repeated use of the same melt. In the TGZM method, by programmatically changing the process parameters is possible to control the properties and structural perfection of multicomponent heterostructures of AIIIBV compound.

2. Theoretical analysis
For calculate the lattice constant a(x, y, z), and the bandgap (E₉) using equation from [10]. The InₓAlᵧGa₁₋ₓ₋ᵧPₑ₁₋ₓ₋ₓ₋ₑ₀/GaAs heterostructures even with a slight increase concentration of indium (x) isopериodic line shifted to the region of high phosphorus concentrations (figure 1). This is important, as in a quaternary AlGaPAs solid solution for matching lattice constant of the epitaxial layer and the GaAs substrate required the small amount of phosphorus and high partition ratio, therefore, growing by TGZM method without feeding is difficult. Thus, to varying the composition of the solid phase is needed feeding of the liquid phase with strongly segregate components, for example, P and Al.
Figure 1. Concentration dependences: isoperiodic lines (red lines), the bandgap (green lines), the value of x given on the curves, dots indicate the experimental data.

At tightening the requirements for the matching ratio of the CTE of the layer and the substrate, area of the isoperiodic compositions on y is narrowed. Calculations showed that usually CTE of quinary solid solutions less than that of GaAs, and the difference of CTE increases with increasing distance of the composition of the solid solution from the composition of a binary compound. When δa = 0.2, then cooling heterostructure from T epit (1100 K) to room temperature leads to rise the difference between the lattices constants of the substrate and epitaxial layer less than 0.1%.

Figure 1 shows the functions of the bandgap $E_g$ of the compositions (green lines). It is seen that $E_g$ rise with increasing y for certain x.

3. Experimental part
Growing InAlGaPAs/GaAs heterostructure performed by TGZM method. As a substrate used monocrystalline gallium arsenide wafers without doping, Si-doped with concentration $1 - 5 \times 10^{18}$ cm$^{-3}$ (n-type) and Zn-doped with concentration $1 - 8 \times 10^{18}$ cm$^{-3}$. Diameter wafers was 50 nm with planes orientation (100) and (111). Plates polished and subjected to chemical etching to remove the outer surface layer. Processing performed in etchants: HCl:CrO$_3$ = 3:1 or H$_2$SO$_4$:H$_2$O$_2$:H$_2$O = 3:1:1.

The thickness of the substrate after the treatment was 400-450 μm. The thickness of the gallium zone varied from 10 to 200 μm. At the growth of thin (less than 10 μm) layers, InP, GaP, and GaAs plates were used as additional feeding. In order to obtain thick (more than 10 μm) layers of InAlGaPAs solid solutions, were used previously synthesized InAlPAs polycrystals containing components with a large distribution coefficient (Al, P). The resulting ingot of the polycrystal was cut into plates with a thickness of 500-600 μm.

«GaAs-Ga - polycrystal InAlGaPAs» sandwiches placed in a chamber which was vacuated to $10^{-3}$ Pa, and then inflated hydrogen to 0.5 Pa, TGZM process was carried out in a hydrogen stream. Heterostructure InAlGaPAs/GaAs grown at temperatures $837 \leq T \leq 937$ K and a temperature gradient $10 \leq G \leq 30$ K. Choice of temperature is carried out by examining the liquidus temperature for each composition by using visually-thermal analysis «in situ» by the method of [11].

The determination of the mismatch between the lattice parameters of the substrate and the layer and also the estimation of the crystal perfection of the heterostructures were carried out by the method of recording X-ray diffraction.

The compositions of the resulting solid solutions were determined on an X-ray microprobe analyzer “Camebax” with an accelerating voltage of 20 kV and a primary beam current of 0.1-1.0 μA. Photoluminescence measurements were carried out in the spectral range from 950 to 1500 nm at a
temperature of 300 K and in liquid nitrogen at 77 K in a cryostat with quartz windows. The source of exciting optical radiation was an injection laser with wavelength of 402 nm and radiation power of 8.5 mW. The photoluminescence was excited from the side of the epitaxial layers.

4. Results and discussion
Investigation and analysis of luminescent properties of quinary solid solutions is conveniently carried out in comparison, starting from binary compounds, increasing number of components to five (figure 2).

![Figure 2](image)

**Figure 2.** Dependence of the intensity of photoluminescence of $A_{\text{III}}B_{\text{V}}$ solid solutions on the composition (bandgap): 1 - p-GaAs, 2 - p-AlGaAs, 3 - p-AlGaPAs, 4 - p-InAlGaPAs/GaAs.

For AlGaAs solid solutions in the region of "direct" transitions, the radiation intensity is almost constant, and a further increase in the content of AlAs in the solid solution causes a rapid decrease in the intensity of radiative recombination.

The physical reason for the sharp decrease in the intensity of radiation in the region of transition to "indirect" compositions is the transition of electrons from the "direct" minimum to "indirect" and the increase, as a consequence, of the fraction of nonradiative recombination.

The use of quaternary solid solutions isoperiodic for binary is reduces the effect of structure defect associated with the mismatch between the lattice parameters of materials mating at the heterointerface and, thereby, increases the efficiency of radiative recombination. As shown in figure 2, the photoluminescence efficiency of epitaxial AlGaPAs layers is practically independent of the composition of the solid solution. In addition, the intensity of radiative recombination increases with the introduction of the fourth component into the ternary solid solution.

Analysis showed that the introduction of the fifth component into the quaternary solid solution makes it possible to obtain, on the basis of binary substrates, strictly isoperiodic and isoexpendic heterostructures and minimizes defectiveness at the heterointerface, which entails a significant increase in the efficiency of radiative recombination and an improvement in the luminescence characteristics of such heterostructures.
Figure 3. The distribution of the density of dislocations along the thickness of the GaAs/In$_x$Ga$_{1-x}$Al$_y$P$_z$As$_{1-z}$ layers: 1 - $x = 0$, $y = 0.35$, $z = 0$; 2 - $x = 0$, $y = 0.35$, $z = 0.05$; 3 - $x = 0.08$, $y = 0.35$, $z = 0.05$; (T = 1133 K, $l = 300 \mu$m, $G = 30 ^\circ$/sec); Changes in the structural perfection of the epitaxial layer and the bordering regions of the substrate, depending on the composition of the film: 4 - reflection from AlGaAs; 5 - reflection from AlGaPAs; 6 - reflection from InAlGaPAs.

Experimental studies (figure 2) showed that for the isoperiodic with the substrate quinary In$_x$Al$_y$Ga$_{1-x-y}$P$_z$As$_{1-z}$/GaAs solid solutions not observed a significant change in the intensity of the photoluminescence when their composition varies, if the band structure of the solid solution does not change.

In figure 3 shows the results of studies of the dislocation density distribution over the thickness of various heterostructures. It is seen that the density of dislocations is the same at all points of a homogeneous composition of the layer (figure 3, curves 1-3), except for regions near the heterointerface.

The dislocation densities in the layer and the substrate usually do not coincide. Moreover, in the layer on the boundary with the substrate, the dislocation density exceeds that in the layer and the substrate. This character of the distribution of the dislocation density along the thickness indicates that, for at large values of the jump in the composition at the ternary layer-binary substrate boundary, the heterojunction is tense.

Measurements of the width of the rocking curve ($B_{1/2}$), carried out on the angle lap of Al$_x$Ga$_{1-x}$As/GaAs heterostructures, confirm this assumption. The results of the ($B_{1/2}$) measurement for Al$_x$Ga$_{1-x}$As solid solutions and the adjacent regions of GaAs substrates are respectively shown in figure 3, curves 4, 5. It can be seen that structural perfection decreases with increasing concentration of aluminum at the heterointerface. Due to the difference in the CTE of GaAs and AlGaAs, on the heterointerface the value of $\Delta a$ at the crystallization temperature is lower than at room temperature. Therefore, after cooling to room temperature, the heterojunction is in a stressed state.

Studies have shown that elastic stresses are concentrated in the region of ~ 10 $\mu$m on both sides of the heterointerface and are absent in the volume of the layer, and their value in the substrate and layer
is practically the same and depends on the composition of the solid solution. Evaluation of the elastic stress level near the Al$_x$Ga$_{1-x}$As/GaAs heterojunction give values not exceeding $1.8 \cdot 10^7$ Pa. The stressed state of the heterojunction can be reduced by decreasing $\Delta a$ due to the addition of the fourth component (P) in Al$_x$Ga$_{1-x}$As (figure 3, curve 5) and InP (figure 3, curve 6). The results of measurements of the dislocations density along the thickness of the Al$_x$Ga$_{1-x}$As$_{1-y}$P$_y$ layers (figure 3, curve 2) showed that the defect area was significantly reduced. The addition of the fourth component reduces the level of residual stresses to $0.5 \cdot 10^7$ Pa in Al$_{0.35}$Ga$_{0.65}$As$_{0.95}$P$_{0.05}$ heterostructures. Consequently, the addition of the fourth component significantly reduces the stresses by providing a lattice matching of the layer and substrate at epitaxial temperatures. However, the defectiveness of the heterointerface, even for isoperiodic compositions of quaternary solid solutions remains quite large, due to the difference in the CTE of the interface layer and substrate, and can be reduced by going to the quinary solution (figure 3, curve 6). In heterostructures based on quaternary solid solutions in which the lattice parameters of the mating materials under epitaxy temperatures coincide, the main source of defects heterojunctions are the thermal stresses caused by the difference in CTE. Thermal stresses are removed by introducing the fifth component. In figure 3 shows the distribution of the dislocation density over the thickness of the In$_x$Al$_{1-x}$P$_y$Ga$_{1-y}$As$_{1-z}$/GaAs layers (curve 3). It can be seen that the introduction of a small addition of In ($x < 0.1$) almost completely nullifies the defect transition range.

Consequently, in quinary solid solutions, due to the matches of lattice parameters and CTE, it is possible to obtain an "ideal" heterocomposition (in which both misfit dislocations and stresses are absent). However, in such cases, the quality of the substrate material plays an important role, since the main contribution to defect formation in quinary heterostructures will be the inheritance of defects from the substrate. Thus, in the epitaxy of quinary solid solutions, the requirements on the quality of the substrate material significantly increase.

5. Conclusions

InAlGaPAs/GaAs quinary solid solutions, with controlled thickness, composition, and structural perfection can be grown in a temperature gradient field from the liquid phase. A homogeneous distribution of the components across the thickness was achieved using recrystallising source InAlPAs. The main parameters determining the quality of the surface, structural perfection and luminescent properties of heterostructures are the thickness and composition of the liquid zone, temperature and temperature gradient of the TGZM process.

Quinary InAlGaPAs/GaAs heterostructures have high crystalline perfection and better luminescence characteristics in comparison with the corresponding ternary and quaternary heterostructures, and therefore are more preferable for highly efficient devices based on radiative recombination.

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