

Obtaining solid solutions of InGaAsPInGaAsP solid solutions in the spinoidal decomposition region

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Abstract. Technology for growing layers of InGaAsP solid solutions with $E_g \sim 1.0 - 1.2\text{ eV}$ on InP substrates in the spinodal decomposition region by the metalorganic vapour phase epitaxy (MOVPE) technique has been developed. Results of investigation of the obtained solid solution layers by the methods of photoluminescence, reflectance anisotropy spectroscopy and fractal analysis are presented.

1.Introduction

The photovoltaic converters for laser radiation with wavelength about $1.06\text{ }\mu\text{m}$ (the local minimum of absorption losses in the Earth's atmosphere), are the most perspective for the free-space power transmission with laser power up to 10 kW . These converters may be used in outer space. The most perspective heterostructure for laser-radiation detector is shown in Figure 1.[1]

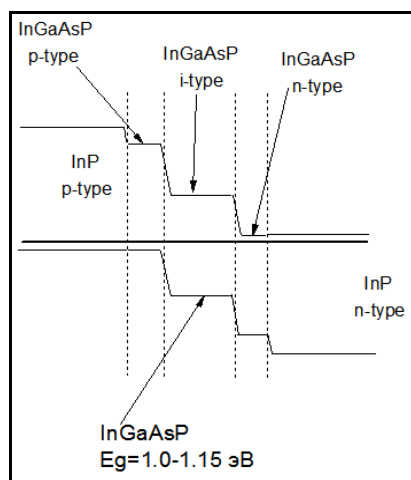


Figure 1. Band diagram of the laser-radiation detector

The photodetectors should be fabricated of the direct band-gap materials with lattice perfection and high mobility of generated charge carriers. The most appropriate material for photodetectors of laser radiation with wavelength $\lambda = 1064$ nm (1,165 eV) is the InGaAsP solid solution, isoperiodic with InP, having the band gap 0.95 – 1.15 eV (300K). However, it is known that these solid solutions grown at 600 - 625°C fall within the spinodal region [2], that complicates obtaining the photoactive layers with the optimal thickness of 1-2 μm .

2. Experimental details

First, the range of spinodal region for InGaAsP solid solutions, isoperiodic with InP, grown at 600°C, has been redefined.

Our calculations were performed within the theory of quasi-regular solutions [3], using the equations and parameters of K.Onabe [2]. According to these calculations, there exists a wide region of spinodal decomposition in the above mentioned system at 600°C. Figure 2 shows that the solid-solution lattice matched to InP with 0.9 - 1.05 eV band gap fall within the spinodal region. [3-7]

Thus, our calculations confirm correctness of location of the boundaries of the spinodal decomposition region.

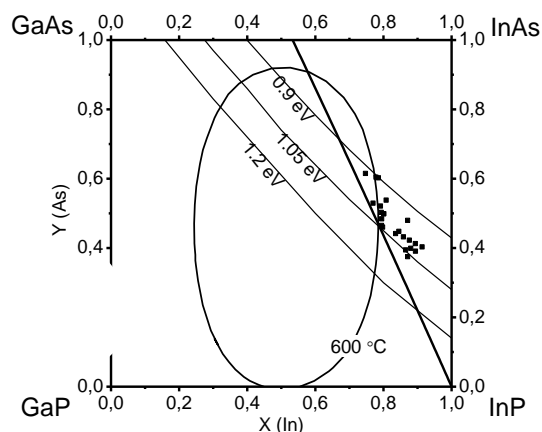


Figure 2. Composition square of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ solid solutions with line of lattice-matched with InP solid solution compositions, spinodal isotherms for 600°C [2] and isobandgap for 0.9 - 1.2 eV lines calculated with parameters from [3]. Dots indicate compositions of specimens obtained in the present work.

Fabrication of the solid-solution layers and heterostructures

To estimate the appropriate growth parameters for fabrication of solid solutions with required composition, the investigations, including determination of growth temperature, temperature of metal-organic compound precursors, III/V molar ratio, and total hydrogen flow were carried out.

All the epitaxial layers were grown on the AIXTRON AIX-200 installation by the metalorganic vapour-phase epitaxy on n-type InP(001) substrates with misorientation of 4° towards (111) at growth temperature 600°C and 100 mbar reactor pressure [8]. Hydrogen, purified through the palladium filter with a dew point of not worse than -100°C was used as a carrier-gas. The total hydrogen flow through the reactor was equal to 5 slpm [8]. The temperature of gallium and indium precursors-triethylgallium (TEGa) and triethylindium (TEIn) – was 17°C. Arsine (AsH_3) and phosphine (PH_3) were used as precursors of V-group elements. The experiments have shown that, to obtain the high-quality samples, the PH_3 flow should be several dozens of times higher than the AsH_3 flow, that is caused by its weak decomposition at 600°C (Figure 3) [9].

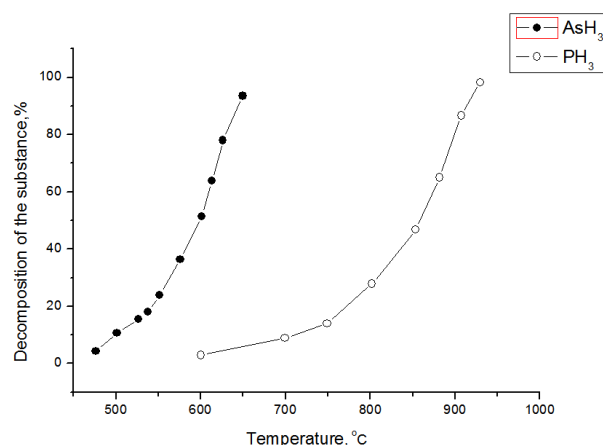


Figure 3. Dependence of AsH₃ and PH₃ pyrolytic decomposition on temperature [9].

The dependence of layer growth rate on III/V molar ratio was studied (see Fig.4). Experimental results show that growth rate of GaInAsP ($E_g \sim 1.0\text{--}1.15$ eV) decreases when III/V molar ratio grows up.

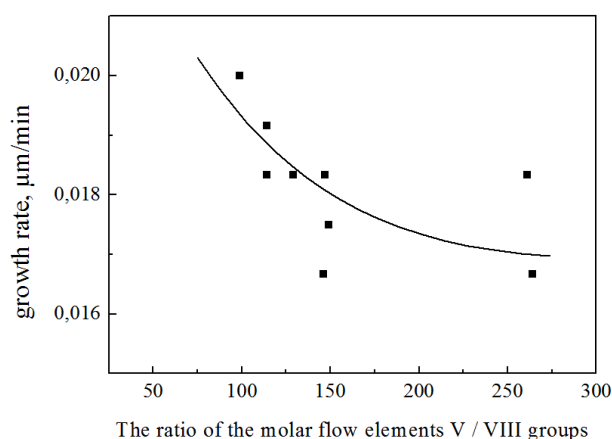


Figure 4. Dependence of GaInAsP layer growth rate ($E_g \sim 1.0\text{--}1.15$ eV) on III/V molar ratio.

Lattice perfection of the obtained samples was controlled by X-ray diffraction and photoluminescence (PL). The X-ray diffraction technique allows to estimate lattice mismatch (peak position on the rocking curve) and lattice perfection (peak half-width). The position and half-width of PL peak allow to determine band gap (E_g) and to characterize material quality respectively.

The X-ray diffraction rocking curve and the PL spectrum of the best GaInAsP sample are shown in Figure 5. The half-width of rocking curve ($\Delta\alpha$) is 0.01° , maximum PL intensity (see in Figure 6) is 40000 y.e., which is close to the best results obtained for InGaAsP samples with required band gap. Thus, analysis of the experimental data allowed to determine optimal parameters for obtaining GaInAsP solid solutions with $E_g \sim 1.0\text{--}1.15$ eV:

- III/V molar ratio -300;
- Phosphine (PH₃) flow -95 splm;
- Triethylgallium (TEGa) flow- 29 splm;
- triethylindium (TEIn) flow- 113 splm;
- Arsine (AsH₃) flow- 1 splm.

Growth rate - $1.5 \mu\text{m}/\text{hour}$, layer thickness - $1.5 \mu\text{m}$.

The layer material composition was determined by the X-ray spectral analysis, layer thickness and surface defects – by scanning electronic microscopy (SEM), surface roughness – on atomic-force

(AFM) and electronic microscopes. To evaluate the material quality, the following techniques were applied: PL, reflectance anisotropy spectroscopy and multifractal analysis of the surface. This paper summarizes results of these investigations, the details are presented in [8,10].

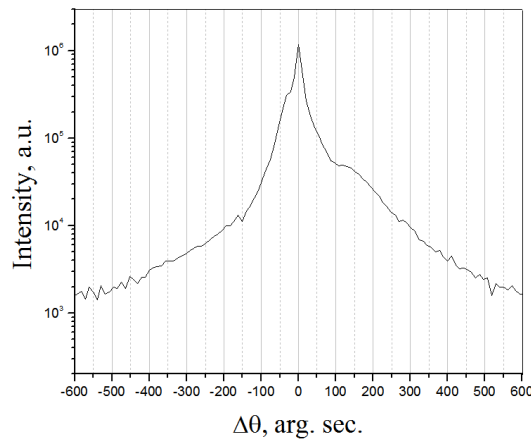


Figure 5. X-ray diffraction rocking curve

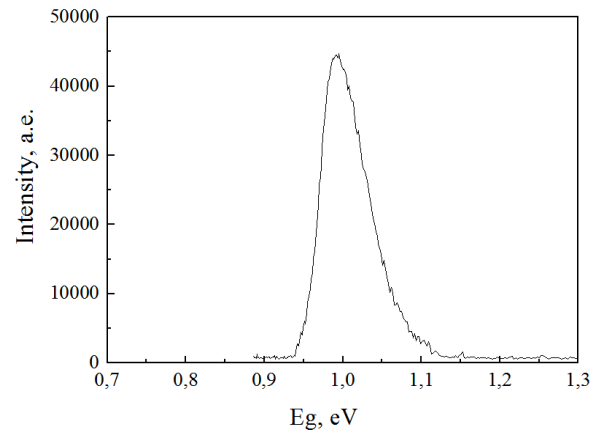


Figure 6. The photoluminescence spectrum ($T=300$ K) GaInAsP with $E_g \sim 1.0$ -1.15 eV.

3. Results of investigations

Multifractal analysis.

The atomic-force microscope images of samples surface (Figure 7,8) show, that small roughness (Table1) is formed on the surface of all the layers. It could appear when cooling, and is caused by the difference in thermal-expansion coefficients of the layer and the substrate. The tension produced in the layer lead to decomposition of solid solution at the surface and breaking of the top layer part. A high roughness (Table 2) is formed only in thick layers practically in the entire depth and partially in the buffer layer, thus relieving stresses in the bulk.

Table1. Small roughness.

Sample No	d, nm	h, nm	Lo , μm	Ld , μm	σ , $\text{din}\cdot\text{cm}^{-2}$
I300	1000	25	0.14	0.145	1.4×10^{10}
I299	500	17	0.12	0.12	1×10^{10}
I298	200	20	0.15	0.16	8×10^9
I297	50	21	0.15	0.15	1×10^{10}

Table2. High roughness.

No	d, nm	h, nm	Lo , μm	Ld , μm	σ , $\text{din}\cdot\text{cm}^{-2}$
I300	1000	45	0.85	0.9	1.4×10^9
I299	500	31	1.2	1.3	3.6×10^8
I298	200	absent			
I297	50	absent			

where σ - tension, h –height roughness, Ld – difference between roughness, Lo – width at the base of the roughness, d – sample thickness.

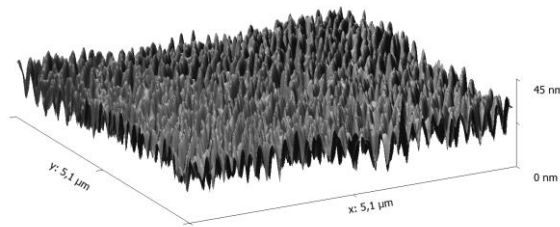


Figure 7. Pictures of the surface of a sample 50nm thick

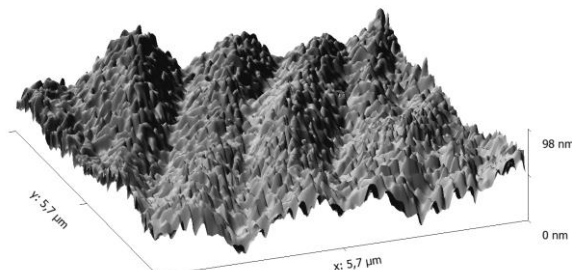


Figure 8. Pictures of the surface of a sample 1000nm thick.

Reflectance anisotropy spectroscopy

To estimate the value of built-in stresses and to define presence of the additional fractions reflectance anisotropy (RA) spectroscopy was used.

Figure 9 shows reflectance anisotropy spectra of surfaces of InGaAsP solid solutions grown on InP(001) substrate for various layer thicknesses. Higher intensity of the InGaAsP spectra, comparing to InP, proves the presence of built-in anisotropic stresses in the layers. The sign of the RA signal indicates that this may be compressive stress in [110] direction or tensile stress in [1-10]. The amplitude of derivative-shape line at approximately 3 eV (optical transitions region $E_1-E_1+\Delta_1$ in InP) is proportional to value of the stress. This amplitude is maximal for the 200 nm layer and decreases for thicker samples. This indicates that the built-in stress is released in layers thicker than 200 nm, that should cause the appearing of anisotropic roughness. This fact was confirmed by AFM observations.

Presence of small spectral features at energies marked by arrows (the positions of optical transitions in InGaAsP) confirms that the InGaAsP of required composition has been formed.

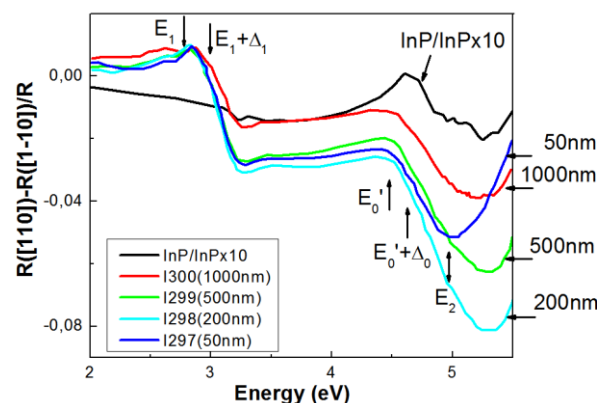


Figure 9. RA spectra of samples I297 - I300 with different thicknesses of InGaAsP layers grown on In(001)

Photoluminescence.

The PL method allows to evaluate material quality – the higher PL signal intensity, the better material: lattice perfection and high mobility of generated charge carriers, long lifetime of carriers. Analysis of the PL spectra shows that at layer thicknesses under 100-200 nm the PL intensity raises with increasing thickness. That is evidence of improvement of material quality (diffusion length increases, influence of surface recombination reduces). At higher thicknesses, the PL intensity decay

takes place, which confirms the inferences about the spinodal decomposition based on reflectance anisotropy spectroscopy and multifractal analysis data (Figure 10).

Basing on the performed investigations, the 1000 nm ten-layer structure (100 nm each layer) (I313) has been fabricated. The PL intensity magnitude of this structure has increased by 3 orders as compared to that of the 1 μm monolithic structure. Figure 11 presents the PL spectrum of this structure.

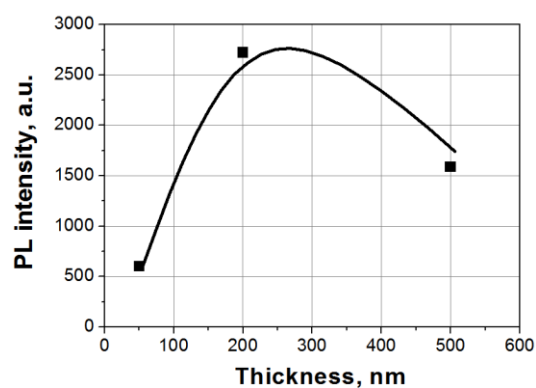


Figure 10. Dependence of the PL intensity on thickness.

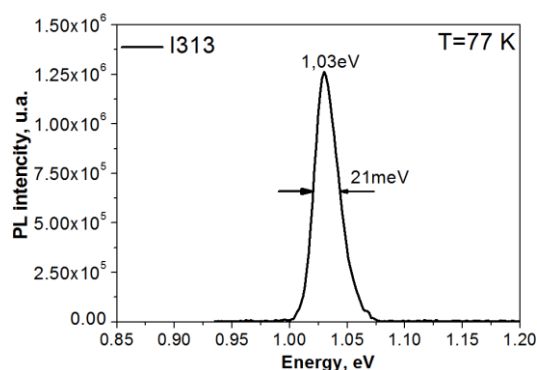


Figure 11. PL spectrum of the best sample I313($\text{In}_{0.8}\text{Ga}_{0.2}\text{As}_{0.46}\text{P}_{0.54}$).

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