

# Investigation of spinodal decomposition of InGaAsP solid solutions grown by the MOCVD technique

A E Marichev<sup>1,2</sup>, B V Pushnyi<sup>1,3</sup> and R V Levin<sup>1,3</sup>

<sup>1</sup> Ioffe Institute, St. Petersburg, Russia

<sup>2</sup> Saint-Petersburg State Electrotechnical University "LETI",  
St. Petersburg, Russia

<sup>3</sup> Submicron Heterostructures for Microelectronics Research and Engineering Center  
of the RAS, St. Petersburg, Russia

E-mail: segregatel@yandex.ru

**Abstract.** Technology for growing layers of InGaAsP solid solutions with  $E_g \sim 1.0 - 1.2$  eV on InP substrates by the MOCVD technique in the spinodal decomposition region has been elaborated. Results of the investigation of solid solution layers by the methods of photoluminescence, reflectance anisotropy spectroscopy and fractal analysis are presented.

## 1. Introduction

Fabrication of high effective photodetectors for powerful conversion of laser radiation requires direct band gap materials with lattice perfection and high mobility of generated charge carriers. Such materials possess high photoluminescence (PL) intensity.

The most appropriate material for photodetectors of laser radiation with wavelength  $\lambda = 1064$  nm (1.165 eV) is the InGaAsP solid solutions isoperiodic with InP, the band gap of which is in the range of 1.0 – 1.15 eV (300 K). However, it is known that these solid solutions grown at 600 – 627°C fall within the spinodal region [1], that complicates obtaining the photoactive layers with an optimal thickness of 1-2  $\mu\text{m}$ .

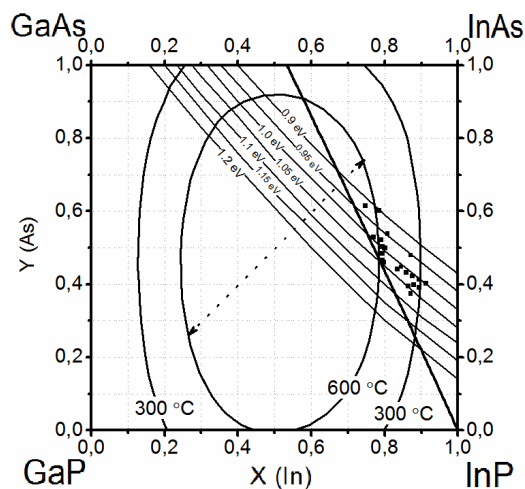
## 2. Experimental details

First, the range of spinodal region for InGaAsP solid solutions isoperiodic with InP was determined. Calculations performed by K. Onabe [1] within the theory of quasi-regular solutions for InGaAsP ones show that there exists a wide region of spinodal decomposition in the system mentioned above at 600°C. Figure 1 shows that, the solid solution with lattice parameters similar to those of InP and the band gap in the range of 0.9 - 1.05 eV falls within the spinodal region.

Calculations performed according to the same model using thermodynamic parameters of Ilegems and Panish [2] give results significantly different from those of Onabe. According to the calculations based on the model of lattice delta-parameter, performed by De Kremu [3], Ipatova [4], and Stringfellow [5], the system of InGaAsP solid solutions at the same temperatures has wider regions of immiscibility than those obtained by calculations made within the model of quasi-regular solutions.

Thus, our calculations have confirmed that the required solid solutions fall within the spinodal region, and it is necessary to design a technology for fabrication of InGaAsP solid solutions layers with parameters (thickness and PL efficiency) appropriate for photodetectors.





**Figure 1.** Diagram of compositions for InGaAsP solid solutions. Spinodal isotherms for 300°C and 600°C, isoenergetic lines for 0.9 - 1.2 eV are constructed using the model from [6] and the isoperiod with InP in the concentration square of GaInAsP solid solutions. Dots indicate compositions of specimens obtained in the present work.

All layers were grown in a MOCVD installation AIXTRON AIX-200 at a pressure of 100 mbar and a temperature of 600°C in a flow of purified hydrogen with a dew point of not worse than -100°C. The total hydrogen flow through the reactor was equal to 5 slpm.

Metal-organic compounds TEGa and TMIn were used as Ga and In sources, respectively, and hydrides Arsin(AsH<sub>3</sub>) and Phosphine(PH<sub>3</sub>) – as As and P sources. Samples doping was not carried out.

The structures were grown on InP(100) substrates with misorientation of 4° towards the (111)A plane (doped with Te,  $n = (1 - 5) \times 10^{18} \text{ cm}^{-3}$ ) on 1 μm thick InP buffer layers.

The layer material composition was determined by the X-ray spectral analysis, the layer thickness – by SEM and the surface quality – by atomic force microscopy. To estimate the material quality, the following methods were applied: PL, reflectance anisotropy spectroscopy and multifractal analysis of a surface.

### 3. Results of investigations

#### 3.1. Reflectance anisotropy spectroscopy.

The following samples of InGaAsP solid solutions have been investigated (table 1):

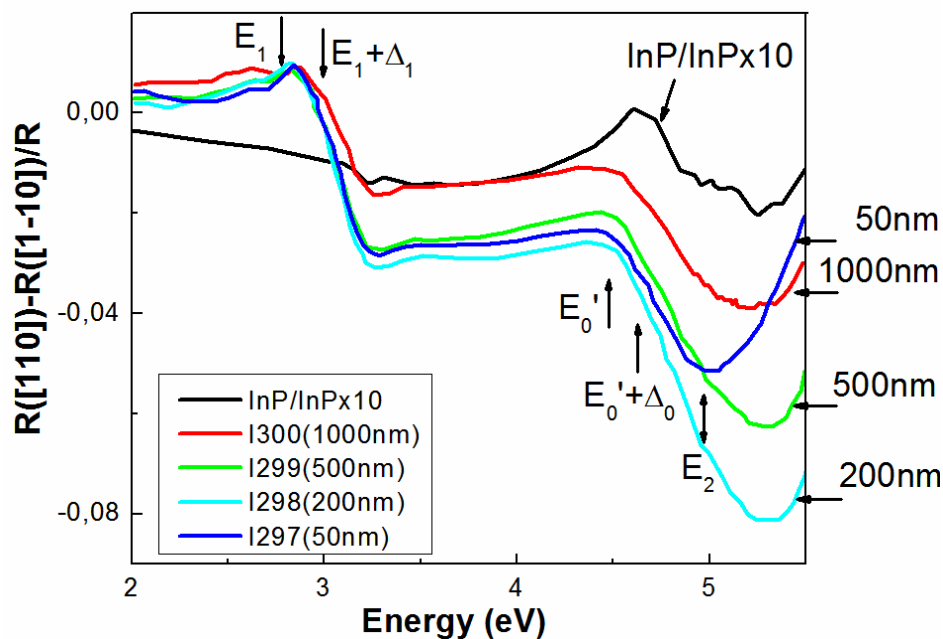
**Table 1.** Characteristics of the tested samples.

Sample No	Thickness, nm	$E_g$ , eV	$\Delta a/a$
I253	1000	1.0	0.015
I255	1000	1.0	$3.88 \cdot 10^{-3}$
I297	50	1.0	0
I298	200	1.0	$< 2.1 \cdot 10^{-3}$
I299	500	1.0	$< 2.1 \cdot 10^{-3}$
I300	1000	1.0	$< 2.1 \cdot 10^{-3}$

Where  $\Delta a/a$  – lattice mismatch between InP and InGaAsP solid solutions,  $E_g$  - the energy band gap.

Reflectance anisotropy (RA) spectra of InGaAsP layers are shown in figure 2, RA spectra of InP are multiplied by 10. Spectra were obtained in air conditions, the samples were covered by a thin layer of natural oxide. As one can see, all samples possess optical anisotropy which is significantly higher than in the case of InP layer. In all the spectra, derivative-like structures are clearly seen in the region of 2.7 - 3.2 eV, which includes energies of  $E_1 - E_1 + \Delta_1$  optical transitions of InP and InGaAsP solid solutions, and also in the region of  $E_0'$  and  $E_2$  optical transitions 4.5 - 5.2 eV. The highest amplitude of

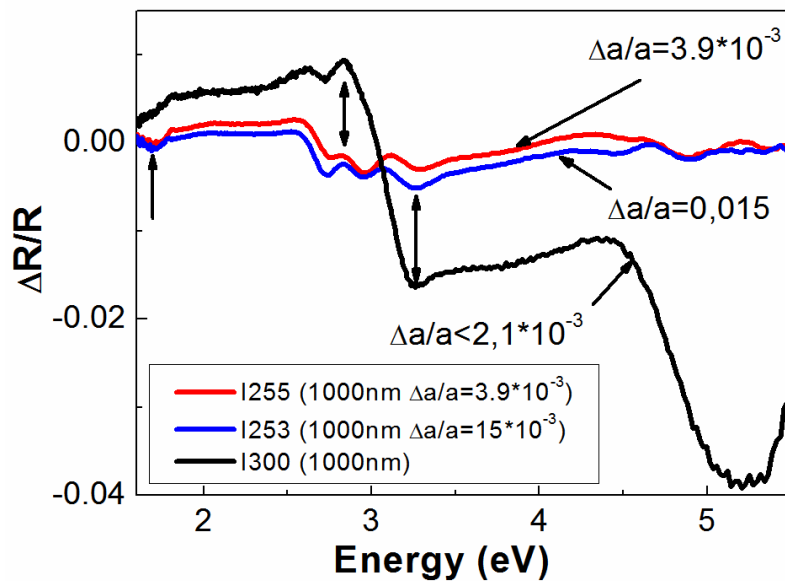
these signals is observed for the 200 nm thick layer. These signals can be associated with anisotropic electric field or anisotropic stress present in the samples, which results in appearing of derivative-like signals. The anisotropic stress gives the same signal and also the background (negative for [110] stress and positive for [1 - 10]). The additional anisotropic background also present in the spectra can be explained by presence of anisotropic roughness on the surface. Presence of peculiarities in the RA spectra of solid solutions at energies of optical transitions in  $\text{In}_x\text{GaAsP}$  (energies are marked by black arrows according to LB) confirms that the obtained layers have the required compositions. Besides the mentioned peculiarities, only ones at the energies of transitions in InP are seen. That means the absence of any other binary compositions in the obtained layer.



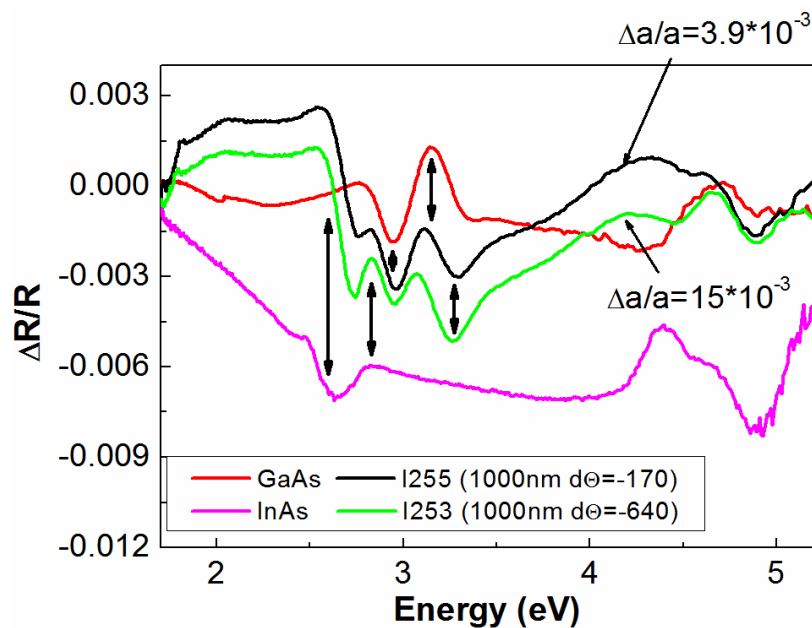
**Figure 2.** RA spectra for the samples I297 - I300 of InGaAsP layers grown on In(001) of different thicknesses

Figure 3 presents the RA spectra of  $1\mu$  thick films (I253, I255 and I300). A substantial weakening of the I253 and I255 spectra amplitudes indicates the decrease of the anisotropic relief of the surface and of a stress in the films. Besides, additional peculiarities appeared in the spectral region of 2.5 - 3.3 eV. In figure 4, these spectra are compared with those of the (001) surfaces of the (001) oxidized surfaces of doped GaAs and InAs. Black arrows indicate peculiarities present in the I300 sample spectrum (2.89eV – InGaAsP and 3.28eV – InP). The peculiarities mentioned above are associated with the  $E_1 - E_1 + \Delta_1$  transitions in the mentioned compounds. Thus, it can be said that GaAs and InAs binary compounds are present in the I253 and I255 films.

Thus, it is established that there is no spinodal in layers (I297-I300), and the layers have a uniform composition, but stresses inducing changes in the surface relief are observed. In the layers of 1000 nm thick I253 and I255, inclusions of different fractions are observed, i.e. decomposition of the solid solution is present.



**Figure 3.** RA spectra of 1000 nm thick samples of InGaAsP layers grown on In(001)



**Figure 4.** RA spectra of 1000 nm thick samples of InGaAsP layers grown on InP(001). Comparison with RA spectra of (001) naturally oxidized surface of GaAs and InAs samples with  $n \sim 2 \times 10^{18} \text{ cm}^{-3}$  doping.

### 3.2. Multifractal analysis.

According to the data of the multifractal analysis of the atomic force microscope images of samples surface, it is seen that a small roughness (Table 2) is formed on the surface of all layers. Probably, its appearance takes place after cooling, and appearing tension results in solid solution decomposition on the surface and a break of the top layer part. A high roughness (Table 3) is formed only for thick layers practically in the entire depth and partially in the buffer layer relieving stresses in the bulk, which improves the layer quality.

**Table 2.** Small roughness.

Sample No	$d$ , nm	$h$ , nm	$L_o$ , $\mu\text{m}$	$L_d$ , $\mu\text{m}$	$\sigma$ , $\text{din}\cdot\text{cm}^{-2}$
I300	1000	25	0.14	0.145	$1.4 \times 10^{10}$
I299	500	17	0.12	0.12	$1 \times 10^{10}$
I298	200	20	0.15	0.16	$8 \times 10^9$
I297	50	21	0.15	0.15	$1 \times 10^{10}$

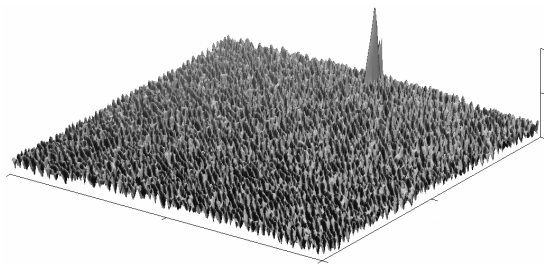
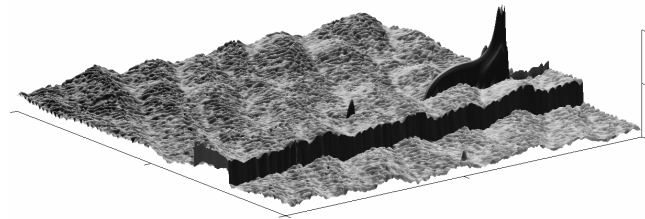
where  $\sigma$  - tension,  $h$  –roughness height,  $L_d$  – difference between roughnesses,  $L_o$  – width at the base of the roughness,  $d$  – sample thickness

**Table 3.** High roughness.

No	$d$ , nm	$h$ , nm	$L_o$ , $\mu\text{m}$	$L_d$ , $\mu\text{m}$	$\sigma$ , $\text{din}\cdot\text{cm}^{-2}$
I300	1000	45	0.85	0.9	$1.4 \times 10^9$
I299	500	31	1.2	1.3	$3.6 \times 10^8$
I298	200	absent			
I297	50	absent			

where  $\sigma$  - tension,  $h$  –roughness height,  $L_d$  – difference between roughnesses,  $L_o$  – width at the base of the roughness,  $d$  – sample thickness.

The tension is most effectively lowered in the sample (I300) by forming a high roughness. Figures 5 - 6 present pictures of typical surfaces obtained by an atomic force microscope.

**Figure 5.** Pictures of the surface of a 50 nm thick sample**Figure 6.** Pictures of the surface of a 1000 nm thick sample.

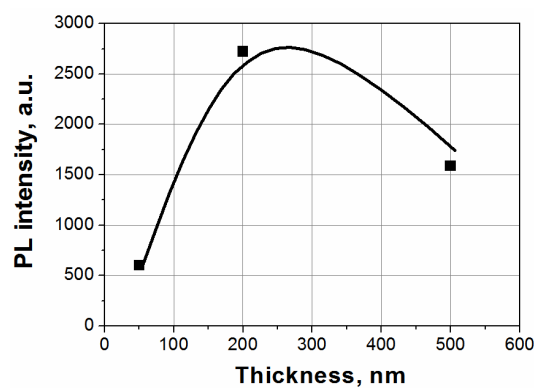
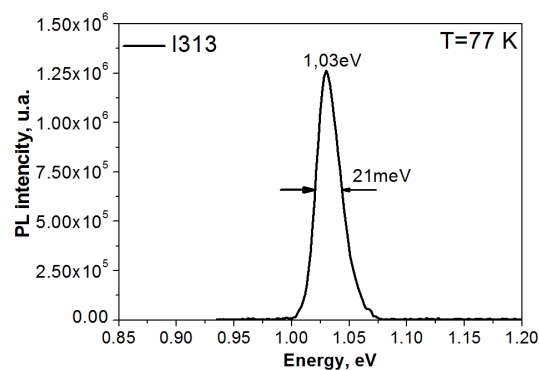
Data of the multifractal analysis do not contradict to the observations of the reflectance anisotropy spectroscopy: stresses grow with layer thickness but the solid solution decomposition is absent. At the layer thickness greater than 200 nm, the surface roughness becomes high, stresses are relieved and the solid solution decomposition is probable.

**3.3. Photoluminescence.** The PL method gives us information on the material quality. The higher the PL intensity, the more perfect is the material. Table 4 presents the results of the PL investigations of the grown samples.

**Table 4.** Results of the PL investigations of the grown samples.

Sample No	Thickness, nm	$\Delta a/a$	PL intensity (a. u.)	FWHM PL (meV)
I253	1000	0.015	694,3	20
I255	1000	$3.88 \times 10^{-3}$	1875	10
I297	50	-	601,9	28
I298	200	$< 2.1 \times 10^{-3}$	2722	20
I299	500	$< 2.1 \times 10^{-3}$	$1,59 \times 10^5$	20
I313	(InGaAsP = 100 nm) 10 replications	-	$1,2 \times 10^6$	21
I314	(InGaAsP = 100 nm/InP 20 nm) 7 replications	-	$9,8 \times 10^5$	24

where -  $\Delta a/a$  – lattice mismatch between InP and InGaAsP solid solutions, PL intensity – photoluminescence intensity for solid solutions, FWHM PL – the full width at a half maximum photoluminescence.

**Figure 7.** Dependence of the PL intensity on the thickness.**Figure 8.** PL spectrum of the best sample I313(In<sub>0.8</sub>Ga<sub>0.2</sub>As<sub>0.46</sub>P<sub>0.54</sub>).

Analysis of the PL spectra confirms the observations of the previous investigations – with growing layer thickness up to 100 - 200 nm (figure 7), the solid solution spinodal decomposition is not observed, the PL intensity rises, and the PL intensity decay takes place.

On the basis of all investigations, a structure with a layer thickness of 1000 nm composed of 10 100nm thick layers (I313) has been fabricated. The PL intensity of such a structure has increased by 3 orders of magnitude. Figure 8 presents the PL spectrum of this structure.

### Acknowledgements

The authors thank N.M. Shmidt, A.B. Gordeyeva, P.N. Brunkow and S.I. Troshkov for their help in the research and discussion of the results.

This work has been supported by the Russian Science Foundation, grant No 14-29-00178.

### References

- [1] Onabe K 1982 *Jpn. J. Appl. Phys.* **21** 797
- [2] Panish M B, Ilegems M 1972 *Paramon Press* **7** 39
- [3] de Cremoux B 1982 *J. Physique* **43** 5

- [4] Ipatova I P, Shchukin V A, Malyshkin V G, Maslov A Yu and Shchukin V A 1993 *Semiconductors* **27** 1062
- [5] Stringfellow G B 1982 *J. Cryst. Growth* **58** 194
- [6] Shim K, Rabitz H 1999 *Journal Of Applied Physics*. **85** 7705