

# Influence of baking on the photoluminescence spectra of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ solid solutions grown on InP substrates

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The influence of thermal treatments on the photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  epitaxial layers of various compositions grown by LPE on InP substrates has been studied. To prevent the epitaxial layers from degradation, due to phosphor evaporation during the baking, their surface was covered by spin-on  $\text{SiO}_2$  layers. The photoluminescence spectra did not change for solid solutions whose compositions were near InP and InGaAs. For compositions in the middle of the lattice-matched region, the variations were very noticeable because the appearance of additional peaks in the luminescence spectra. This could be related to the decomposition of those solid solutions whose compositions lie inside a theoretically predicted miscibility gap.

**Keywords:** InGaAsP; solid solution; miscibility gap; decomposition and photoluminescence.

Se ha estudiado la influencia de diferentes tratamientos térmicos sobre los espectros de fotoluminiscencia de capas epitaxiales de  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  con diferentes composiciones, crecidas sobre sustratos de InP, mediante la técnica de epitaxia en fase líquida. El espectro de fotoluminiscencia de soluciones sólidas de composición cercana al InP o InGaAs no cambió después del recocido. Para composiciones cercanas al centro de la región en que la constante reticular de las capas es igual a la del InP, el cambio fue muy notorio debido a la aparición de un pico adicional en el espectro de fotoluminiscencia. Esto podría relacionarse con la descomposición de aquellas soluciones sólidas cuya composición esta dentro de una brecha de miscibilidad predicha teóricamente. Para evitar la degradación de las capas epitaxiales, causada por la evaporación de fósforo durante el recocido, su superficie se recubrió con capas de  $\text{SiO}_2$  depositado de una emulsión.

**Descriptores:** InGaAsP; solución sólida; brecha de miscibilidad; descomposición y fotoluminiscencia.

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## 1. Introduction

It is known that in many III-V solid solutions the atoms in the metal and non-metal sub-lattices are distributed randomly and homogeneously [1]. However, in several cases, deviations from the random and homogeneous distribution take place in the III-V solid solutions and these deviations are caused by different reasons [2]. One of such reasons is related to the spinodal decomposition. It is well known from common thermodynamic models that solid solutions are decomposed and lose their homogeneity when the V-shaped dependence of the Gibbs energy on concentration becomes a W-shaped one [3]. As a result, a miscibility gap appears in the phase diagrams of such systems.

Among the different III-V multicomponent solid solutions, a wide miscibility gap exists in the  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_y$  system [4,5]. This gap comprises a big area of the  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_y$  compositions lattice matched to the GaSb and InAs binary compounds, used as substrates to grow these materials. That is why the quaternary  $\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_y$  solid solutions can be grown by liquid phase epitaxy (LPE) on GaSb substrates only in limited composition areas. It has been shown [6,7], that a miscibility gap could exist also in the  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  solid solutions but its extent and boundaries are not well established and differ from author to author [8-11]. However, it is well known, that  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ , whose composition lies well inside the predicted miscibility gap, can be grown using near equi-

librium techniques, for example by LPE. On the other hand, it has been demonstrated that, under certain conditions, attempts to grow  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  inside the miscibility gap could lead to the formation of structures with periodic composition modulation and this has been explained by a spinodal decomposition process [12-15].

It is obvious, that any composition changes of the solid solutions will have an influence on their optical and physical properties. The study of these effects is important from both, the scientific and technological points of view, perhaps the decomposition processes of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  solid solutions are the most interesting because they are widely used in the production of different devices. The present work is devoted to study the possibility of spinodal decomposition of this material due to thermal treatments. For this purpose the influence of high-temperature treatments on the photoluminescent properties of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  epitaxial layers of various compositions grown on InP substrates was investigated.

## 2. Peculiarities of the decomposition and high temperature baking of $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ solid solutions

As noted above, a rather wide miscibility gap may exist in the  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  phase diagram. This gap comprises some solid solution compositions lattice matched to GaAs and InP substrates. However, it is well known, that

$\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  quaternary solid solutions, even those whose composition lie inside the predicted miscibility gap, can be grown on GaAs and InP substrates, for example by LPE. The photoluminescence spectra of these materials are similar to the spectra of binary III-V compounds with "direct" band gap structure and have the same full widths at half maximum. Laser diodes, fabricated on the basis of InGaAsP/GaAs and InGaAsP/InP multilayer heterostructures, can work for a rather long time without any changes of the spectral and threshold characteristics. Thus, it is logical to suppose that some  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  solid solutions are thermodynamically metastable in the usual conditions. During a high-temperature baking the diffusion coefficients in the solid phase increase, accelerating the spinodal decomposition process. These changes in composition must be evidenced by changes in the properties of these materials, for example, in their photoluminescence spectra.

However, during a thermal treatment there is another mechanism of composition variation that could mask the effects of spinodal decomposition. In a crystal containing components with large partial vapor pressures composition changes could take place due to intensive evaporation of these elements. Obviously, the largest changes, among the III-V solid solutions excluding the nitride systems, will take place in the phosphor containing systems. Phosphor evaporates very easily from the surface of InP and InP-based solid solutions. Since the purpose of this work is to study the possibility of spinodal decomposition of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ , we

have to develop a method to separate the effect of these two mechanisms.

One way to prevent the evaporation of phosphor is to do the thermal treatment in a closed ampoule, where a pressure appropriate to suppress the evaporation can be set. However, this method is technically rather complicated.

It is known that, according to Raoult's law, the partial vapor pressure of any element over the solid or liquid phase is proportional to its concentration in the corresponding phase. Therefore, in  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  solid solution lattice matched to InP, the most intensive evaporation of phosphor should be observed at  $x = 0$  and  $y = 0$ , *i.e.*, for InP. Consequently, if some method can be used to eliminate the phosphor evaporation from the surface of InP, automatically the same method can be applied to a solid solution of any other composition.

### 3. Experiments

In order to estimate the influence of high-temperature baking on the quality of InP surfaces we have baked samples for five hours at different temperatures. The baking and growth experiments were done in an usual LPE reactor under a Pd purified hydrogen flow. In both, the baking and growth processes, which will be described later, the  $\text{H}_2$  flow was precisely set by a mass flow controller because it has a strong influence on phosphor evaporation [16]. In all the experiments the  $\text{H}_2$  flow was 20 sccm. The results are illustrated on Fig. 1 with pho-

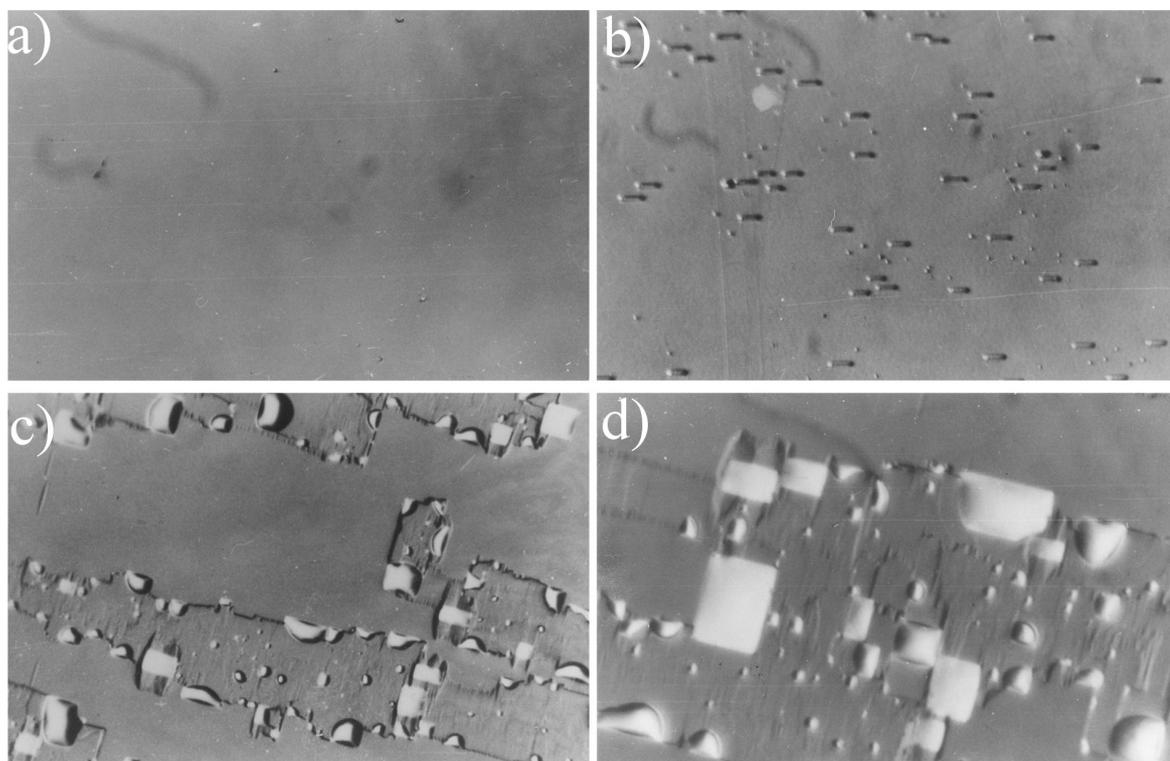


FIGURE 1. Microphotographs of InP surfaces a). Before baking. Baked for 5 hours at b). 200°C, c). 500°C and d). 750°C.

tographs showing the surfaces of InP substrate after baking at 200, 500 and 750°C. A dramatic deterioration of the surface occurs even after the 200°C, five hours baking, as can be seen from the indium-covered areas formed because of P evaporation, these areas increase with baking temperature.

Spin-on SiO<sub>2</sub> layers were deposited to protect the surface of substrates or epitaxial layers from phosphor evaporation. After spin-on deposition at 3000 rpm, the SiO<sub>2</sub> films were dried at 90°C for 15 minutes and then baked in air at 350°C for 1 min. The thickness of the SiO<sub>2</sub> layers was around 1 μm.

The growth processes of the epitaxial layers were carried out in a usual horizontal LPE reactor. The InP (100) n-type substrates used in the experiments had an area of 1 × 1.5 cm<sup>2</sup> and a charge carrier concentration of 10<sup>17</sup>–10<sup>18</sup> cm<sup>-3</sup>. The nominal composition of the quaternary epitaxial layers and their corresponding lattice mismatch, as measured with a four crystal X-ray diffractometer, are shown in Table I. After epitaxial growth, the samples were cleaved into three parts. One of these was not further processed and was used as a control sample. The two remaining parts were covered with SiO<sub>2</sub> films and were baked at different temperatures for 5 hours. After the thermal treatments, the protective films were removed by HF.

The photoluminescence was excited with the 574 nm line of a 100 mW Ar laser and the spectra were recorded using a 0.5 m monochromator and standard synchronous detection techniques.

#### 4. Results and discussions

For the samples covered with SiO<sub>2</sub> protective films the surface quality of InP practically did not change and remained mirror-like after a baking process of 5 hours at temperatures up to 750°C. The intensities of the main peak of the photoluminescence spectrum of epitaxial InP did not change after the thermal treatment. These results show that SiO<sub>2</sub> films reliably protect the surface of InP and consequently also In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub> solid solutions from composition changes, due to evaporation, during the baking processes at temperatures up to 750°C.

On the other hand, significant changes in the photoluminescence spectra were observed for the In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub>

TABLE I. Parameters of the samples at the room temperature.

Sample No.	Peak of the photoluminescence spectrum at 77 K	Lattice mismatch,	In <sub>1-x</sub> Ga <sub>x</sub> As <sub>y</sub> P <sub>1-y</sub> composition	
	$\lambda_{\max}$ , μm	$\Delta a/a$	$x$	$y$
1	1.02	$4.6 \times 10^{-4}$	0.08	0.17
2	1.13	$-9.1 \times 10^{-4}$	0.17	0.37
3	1.22	$9.0 \times 10^{-4}$	0.26	0.55
4	1.32	$-16.3 \times 10^{-4}$	0.31	0.67
5	1.44	$-10.4 \times 10^{-4}$	0.4	0.85
6	1.53	$-2.3 \times 10^{-4}$	0.45	0.97

epitaxial solid solutions after baking. The photoluminescence spectra of baked and non-baked samples of In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub> with various compositions are presented on Figs. 2-7. The spectra were measured at 77 K. The annealing temperatures are shown on each spectrum along with the lattice mismatch of the non-baked samples. From Fig. 2 it is seen, that the baking processes do not influence the general shape of the emission spectrum of In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub> whose composition is close to InP. For these samples the intensity maximum lies at a wavelength of  $\lambda_{77\text{K}}^{\max} = 1.02 \mu\text{m}$ . In a sample whose composition is farther away from InP and that has  $\lambda_{77\text{K}}^{\max} = 1.13 \mu\text{m}$  a long wavelength shoulder appears on the spectrum after baking at temperature 500°C (Fig. 3). After a similar baking process of the sample with  $\lambda_{77\text{K}}^{\max} = 1.22 \mu\text{m}$  a second line with maximum at  $\lambda = 1.62 \mu\text{m}$  can be seen in its emission spectrum (Fig. 4). In the samples with

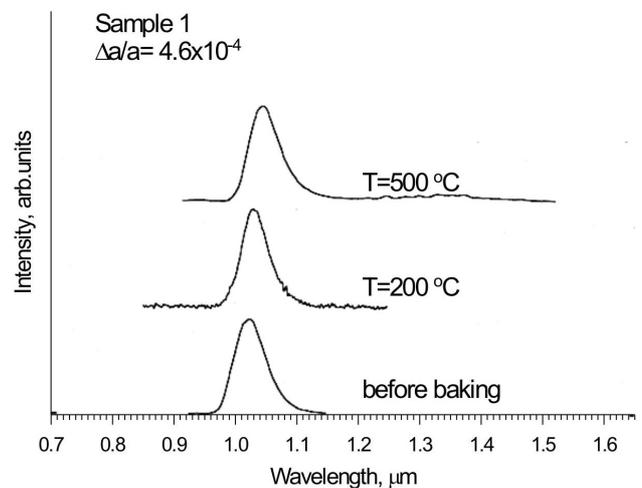


FIGURE 2. Photoluminescence spectra of In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub> with  $\lambda_{77\text{K}}^{\max} = 1.02 \mu\text{m}$ , before and after baking.

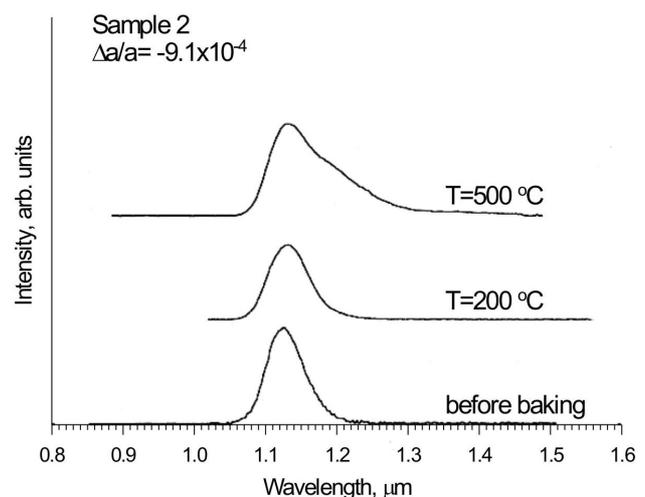


FIGURE 3. Photoluminescence spectra of In<sub>1-x</sub>Ga<sub>x</sub>As<sub>y</sub>P<sub>1-y</sub> with  $\lambda_{77\text{K}}^{\max} = 1.13 \mu\text{m}$ , before and after baking.

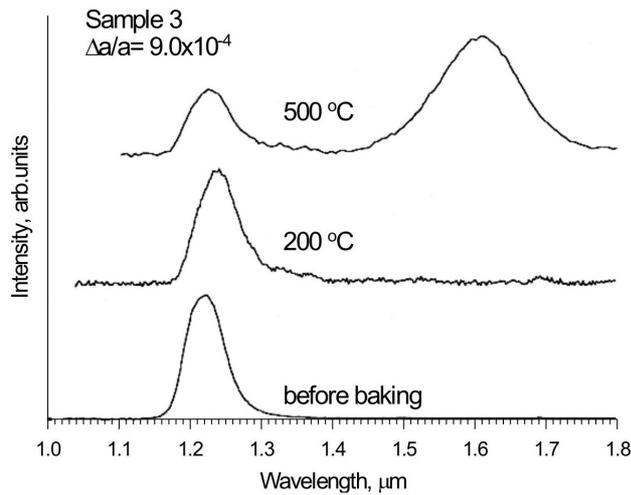


FIGURE 4. Photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  with  $\lambda_{77\text{K}}^{\text{max}} = 1.22 \mu\text{m}$ , before and after baking.

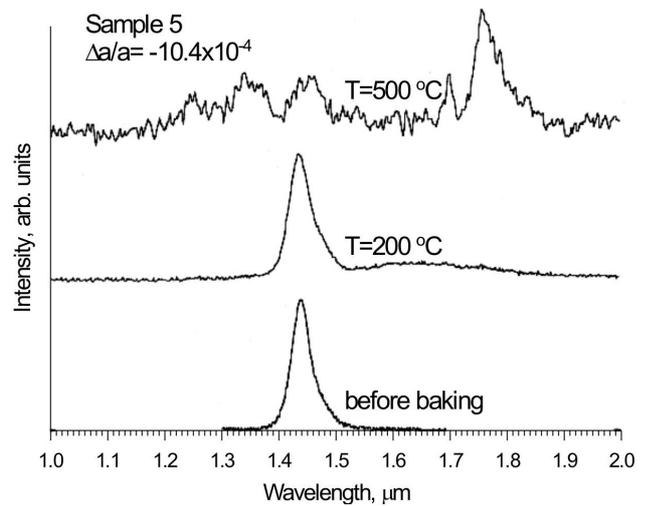


FIGURE 6. Photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  with  $\lambda_{77\text{K}}^{\text{max}} = 1.44 \mu\text{m}$ , before and after baking.

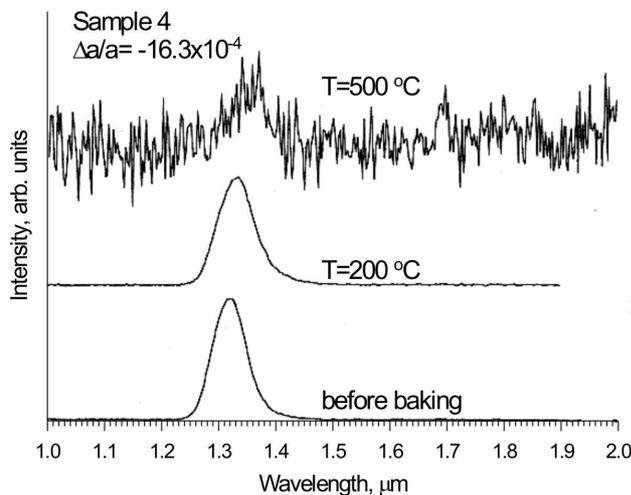


FIGURE 5. Photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  with  $\lambda_{77\text{K}}^{\text{max}} = 1.32 \mu\text{m}$ , before and after baking.

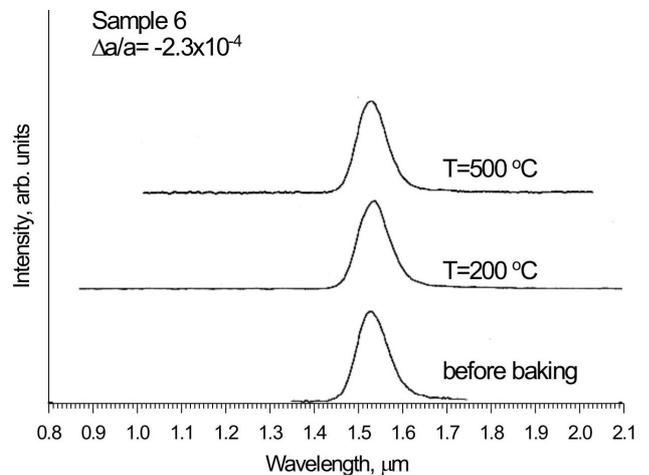


FIGURE 7. Photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  with  $\lambda_{77\text{K}}^{\text{max}} = 1.53 \mu\text{m}$ , before and after baking.

$\lambda_{77\text{K}}^{\text{max}} = 1.32 \mu\text{m}$  and  $\lambda_{77\text{K}}^{\text{max}} = 1.44 \mu\text{m}$ , several weaker, not well resolved lines, appear after baking at 500 °C as shown in figs. 5 and 6. For the last sample with a composition closer to  $\text{In}_{0.48}\text{Ga}_{0.52}\text{As}$  and with a peak at  $\lambda_{77\text{K}}^{\text{max}} = 1.53 \mu\text{m}$ , the emission spectrum again does not change after baking (Fig. 7).

In Fig. 8 the boundaries of the miscibility gap, calculated by different authors, are plotted along with points showing the composition of our samples. The diamonds correspond to the samples where changes in the luminescence spectra has been observed. As can be seen, there are important differences in the location of the boundary as calculated by several authors. The real position is still not well established. It can also be seen in Fig. 8 that only the points corresponding to the samples whose luminescence spectra changed after baking lie inside or near the boundaries of the miscibility gap.

Recapitulating, the photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  changes appreciably after the baking process only in the samples whose compositions lie in the middle region of the InP lattice-matching cross-section. However, no transformations of the spectra are observed for the solid solutions compositions near to InP and  $\text{In}_{0.48}\text{Ga}_{0.52}\text{As}$ . These results could be explained assuming the break up of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  with composition inside the miscibility gap.

It should be noted, that most likely the baking temperature of 500 °C is not high enough to accelerate the diffusion processes in the solid phases so as to produce appreciable changes within 5 hours. However, since the diffusion coefficients in the surface are several orders of magnitude larger than in the bulk, it could be reasonable to expect a faster decomposition process near the surface of the samples. It has been shown [6,7,12,13] that the decomposition of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  solid solutions occurs much faster close to surface than in the bulk of the epitaxial film.

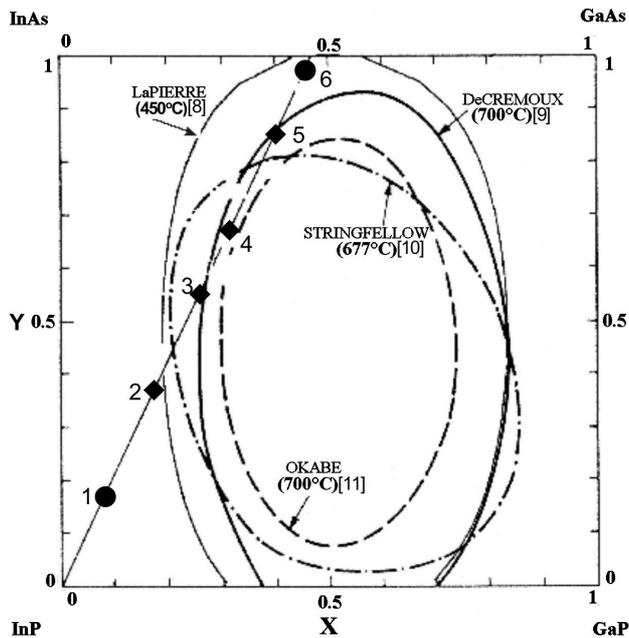


FIGURE 8. Boundaries of the miscibility gap as calculated by several authors [8-11].

It is also known that stresses in the epitaxial layers could facilitate the decomposition processes [17]. In our experiments the difference of thermal expansion coefficients between  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  and the  $\text{SiO}_2$  protective films can introduce additional tensions close to their boundary and, consequently, contribute to accelerate the decomposition processes. Therefore, despite the low temperature and short baking time a decomposition process can take place but in a limited depth beneath the surface. This would be in agreement with theoretical predictions reported in [6,7,17]. Another ob-

servation supporting this assumption is the fact that the X-ray rocking curves of the samples do not change after baking.

## 5. Conclusions

We have developed a method to protect the surface of materials containing volatile components from erosion due to evaporation during baking processes. It was shown that the deposition of a  $\text{SiO}_2$  layer eliminates the surface degradation of samples baked at temperatures as high as  $750^\circ\text{C}$  during up to 5 hr. This technique allowed us to study the influence of thermal treatments on the photoluminescence spectra of  $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$  epitaxial layers grown on InP substrates. In the middle area of compositions, where a miscibility gap is theoretically predicted, the photoluminescence spectra are noticeably transformed but for compositions near InP and  $\text{In}_{0.48}\text{Ga}_{0.52}\text{As}$  there are no changes observed in the emission spectra. We suppose that these transformations are related to spinodal decomposition processes that take place in spite of the relatively low temperature and short baking times used. The decomposition may take place in a limited depth beneath the surface because of the larger diffusion coefficients at the surface of the layers and the additional stresses introduced by the  $\text{SiO}_2$  films used to protect the solid solutions from P evaporation.

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