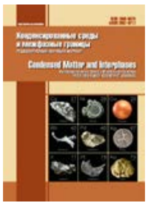

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Technological features of the method of liquid-phase epitaxy when growing InP/GaInAsP heterostructures

M. G. Vasil'ev✉**, A. M. Vasil'ev, A. D. Izotov**✉**, Yu. O. Kostin, A. A. Shelyakin**

Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences,
31 Leninsky prospect, Moscow 119991, Russian Federation

Abstract

Semiconductor devices of quantum electronics based on InP/GaInAsP heterostructures require the creation of non-defective chips for emitting devices and photodetectors. The production of such chips is impossible without a thorough technological study of the growth processes of epitaxial structures. One of the important problems in relation to the growth of such structures is the growth defects associated with the process of dissociation of indium phosphide on the surface during their growth. The aim of the work was the investigation of the process and mechanism of destruction (dissociation) of the surface of indium phosphide substrates in the range of growth temperatures of structures, as well as the study of methods and techniques that allow minimize the process of dissociation of surface of indium phosphide.

The work provides studies of the growth processes of InP/GaInAsP heterostructures, from the liquid phase, taking into account the degradation processes of the growth surface and the mechanisms for the formation of dissociation defects. The schemes of the dissociation process of the InP on the surface of the substrate and the formation of the defective surface of the substrate were analysed. At the same time, technological methods allowing to minimize the dissociation of the surface compound during the process of liquid-phase epitaxy were shown. The original design of a graphite cassette allowing to minimize the dissociation of the indium phosphide substrate in the process of liquid-phase epitaxy was proposed.

Keywords: Heterostructures, Growth defects, Laser diodes, Indium phosphide, Buried heterostructures, Channel in the substrate

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✉ Mikhail G. Vasil'ev, e-mail: mgvas@igic.ras.ru

✉ Alexander D. Izotov, e-mail: izotov@igic.ras.ru

1. Introduction

The process of liquid-phase epitaxial growth is a heterogeneous process occurring at the liquid-solid interface. The analysis of the conditions of contact between the substrate and the nonequilibrium liquid or gas phase [1–3] indicates the complexity of the contact phenomena occurring at the interface. In this regard, the preparation of indium phosphide substrates for epitaxial growth can be of decisive importance for the growth of structures [4, 5] required for manufacturing of devices of quantum electronics. InGaAsP solid solutions are widely used for the production of devices for quantum electronics, laser diodes, superluminescent radiation sources, and photodetectors [6-10]. The main area of application of these devices is systems for transmitting optical signals through quartz fiber [11, 12], fiber-optic sensors for environmental monitoring [12, 13], optical coherence tomography [14, 15], navigation and instrumentation systems [16, 17]. The creation of such devices requires the production of high-quality epitaxial layers of InP/GaInAsP heterostructures on indium phosphide substrates, which, in turn, makes it necessary to pay special attention to the quality of the growth surface of the substrates before epitaxial growth. Such structures are mainly grown as isoperiodic on InP. Particular attention should be paid to the state of the initial InP substrate before and during the liquid-phase epitaxy process in the temperature range of 675–600 °C. Due to the fact that indium phosphide contains a highly volatile phosphorus component in its composition, epitaxial growth leads to dissociation of the substrate with the appearance of characteristic defects in the form of faceted depressions with indium drops (Fig. 1). In the course of epitaxial growth, these defects grow into the epitaxial structure, which leads to the low quality of the manufactured devices.

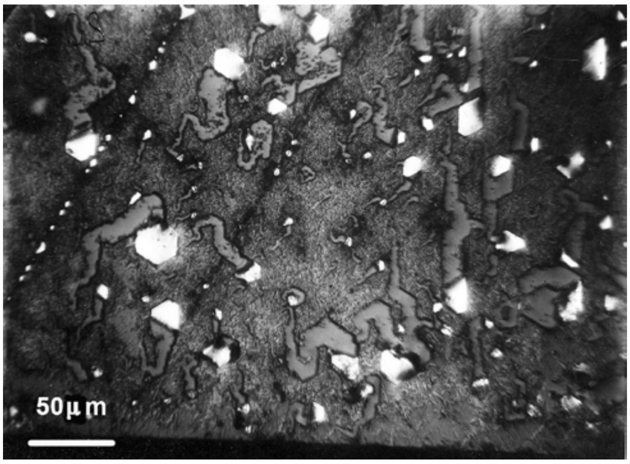

Fig. 1. Dissociation of the indium phosphide on the surface of the plate

The aim of this study was the investigation of the process and mechanism of destruction (dissociation) of the surface of indium phosphide substrates in the temperature range of growth of structures, as well as the study of methods and techniques allowing to minimize the process of dissociation of the surface of indium phosphide.

2. Experimental

Microscopic studies prove the existence of the effect of solution-melt dissolution (SMD) of the indium phosphide substrate during the growth of InP and InGaAsP epitaxial layers by liquid-phase epitaxy (LPE). The SMD effect can manifest itself in the form of depressions with In droplets or grooves with In droplets on the surface of both InP substrates and on layers grown in the InP/InGaAsP system. Subsequently, this effect negatively affects the production of layers in InP/InGaAsP heterostructures. The process of creating semiconductor chips for laser diodes, photodiodes and light-emitting diodes includes the operations required for the application of dielectric masking coatings. Dielectric coatings are used in the manufacture of strip-line laser diodes [18]. It is known [19] that the intensification of phosphate formation on the InP surface leads to the formation of nanosized dielectric films, the resistivity of which reaches 10^{10} Ohm· cm, which sharply reduces the leakage currents through the insulating film and leads to an increase in the quantum efficiency of laser diode radiation and a decrease in dark currents in photodiodes based on InP/GaInAsP heterostructures.

In this regard, it becomes obvious that the surface quality of the grown InP/GaInAsP epitaxial heterostructures becomes decisive in the design of chips for devices.

The formation of a multilayer heterostructure in the InP/InGaAsP system by LPE method starts with an increase in the temperature inside the quartz reactor to 675 °C in an atmosphere of H_2. The substrate is located in a graphite cassette (Fig. 2)

Fig. 2. Graphite cassette for growing layers on InP/InGaAsP on InP substrates

in a substrate holder. The rise in temperature in the range of 600-675 °C occurs in 10 minutes. Then, for 30 minutes, exposure at 675 °C and the onset of a isothermal mode are performed. Then, for 20 minutes, cooling by 10-15 degrees to the onset of growth, which is a temperature of 660 °C. The substrate is kept at an elevated temperature for ~1 hour in an atmosphere of dry H_2 with a dew point of –80 °C.

The InP compound has a crystal structure of the sphalerite type, in the lattice of which, due to the alternation of two types of atoms, there is no inversion symmetry. This leads to the fact that in crystals with the <111> directions axes are polar, which in turn leads to a difference between the A (111) and B (111) planes. The {111} crystallographic plane consists of two geometric planes, each of which contains atoms of only one type, as a result of which atoms of either 3 or 5 groups emerge on the outer surface of the crystallographic planes. Atoms of group 5 (surface B) use only three of the available five valence electrons for the formation of bonds with the lattice and thus have two electrons capable of interacting with particles of the outer phase. Group 3 atoms of surface A use all three valence electrons for the formation of bonds with the lattice. In this regard, B surfaces are more reactive than A surfaces, which leads to the dissociation of indium phosphide during epitaxial growth processes.

The dissociation process is shown in Fig. 3. In the course of experimental work on the growth of heterostructures, we discovered that the formation and movement of an indium drop occurs in a certain direction. In this case, the depression or groove is faceted by the {111} A and {111} B planes simultaneously. In practice, after high-temperature exposure, the substrate is covered with a micro-profile in the form of etching pits resulting from the dissociation of indium phosphide. The effect of the formation of a depression or groove at an elevated temperature as a result of the loss of phosphorus by the surface and the release of a drop of indium will be called the solution-melt dissolution "SMD" effect. The "SMD" effect is shown schematically in Fig. 4. Studies carried out in [20] showed that the {001} A and {111} B planes will grow at a rate of 0.2 μm/°C and 0.4 μm/°C, respectively, and the {111} A plane will grow only at a rate of 0.1 μm/°C. Thus, planes {111} A will prevent the overgrowing of depressions and grooves and facet them along the entire thickness of the grown layer. In this case, from one depression or one groove, two depressions located symmetrically against each other, will be formed (Fig. 5). This is shown schematically in Fig. 6.

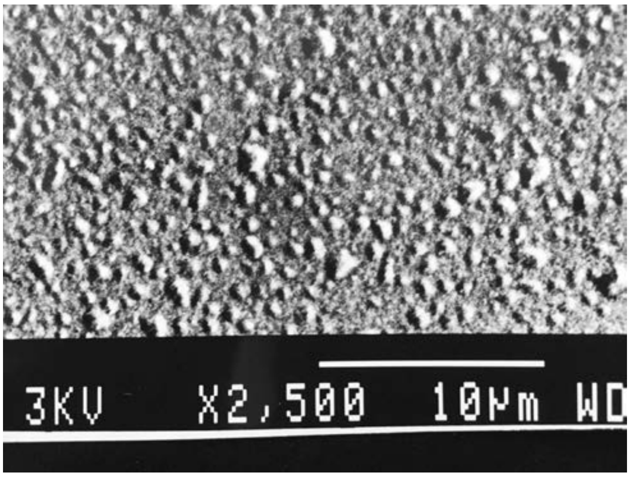

Fig. 3. Indium drops on the surface of InP substrate

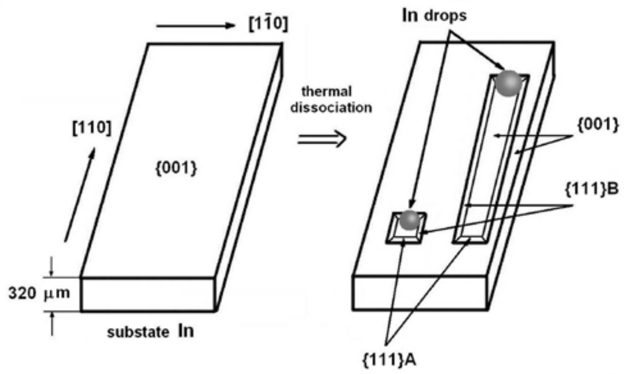

Fig. 4. Scheme of the dissociation of InP on the surface of the substrate

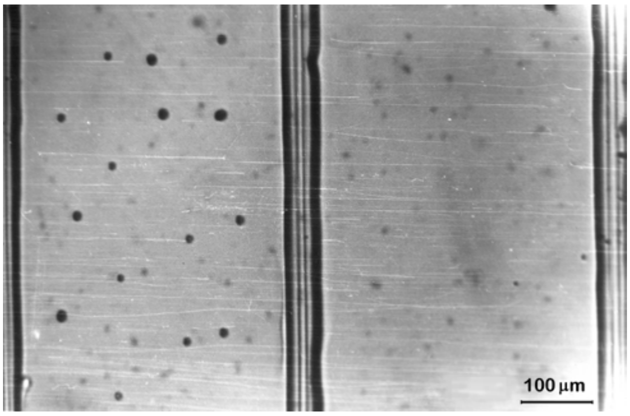

Fig. 5. Growing of InP buffer layer on the surface of the substrate, with dissociation traces

In order to eliminate the “SMD” effect, a number of technological methods were proposed:

– a decrease in the growth temperature of growing epitaxial heterostructures in the InP/InGaAsP system from 675 to 610 °C without affecting the structural properties of epitaxial layers and the electrophysical parameters of future devices;

– optimization of current consumption of H_2 from 10 l/h to 2-4 l/h;

– optimization of the design of the graphite container, which makes possible the provision of an additional quasi-closed volume for the creation of partial pressure of phosphorus during the growth of the InP/GaInAsP heterostructure;

– rapid cooling of the growth system with a growth cassette.

It is known [21] that indium phosphide has significant solubility in the tin melt. In this regard, a special solution-melt of indium phosphide in tin was prepared, placed in a quasi-closed volume of the growth cassette (Fig. 7) and it served as a source of the partial pressure of phosphorus during epitaxial growth. In addition, immediately before the start of the growth process, the indium phosphide substrate was etched with a 50% diluted In-InP melt solution, which allowed the etching of 3 to 5 µm from the damaged indium phosphide layer.

After the end of the growth process, in order to reduce the dissociation of the grown epitaxial layers, the graphite cassette was abruptly cooled at a cooling rate of 20–30 degrees per minute by shifting the heating furnace. The proposed technological process allowed to obtain mirror-smooth layers with a density of growth defects not more than $5\cdot10^2$ cm^{-2}.

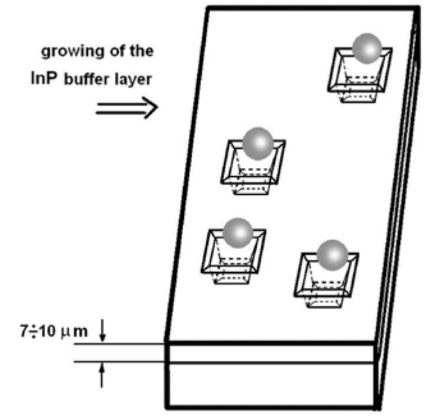

Fig. 6. Scheme of the formation of depressions in the process of growing the InP buffer layer

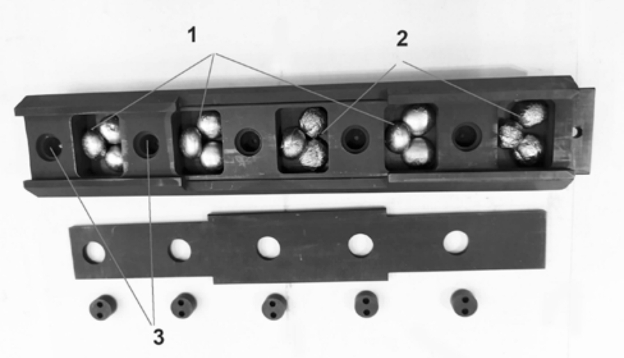

Fig. 7. Graphite cassette with quasi-closed volumes: *1* – solution-melt InP; *2* – solution-melt InGaAsP; *3* – reservoirs for increasing the partial pressure of phosphorus

3. Conclusion

The solution-melt dissolution (SMD) effect is present throughout the growth process by liquid-phase epitaxy in the InP/InGaAsP system on InP substrates. This effect is extremely undesirable and caused by the polarity of the {111} A and {111} B planes, which is clearly manifested during the growth of InP buffer layers. The family of planes {001} and {111} B aligns the depressions and grooves, and the family of planes {111} A with planes {001} and {111} B facets them. As a result of the joining of the {111} planes in the depression, they are cut faceted from both sides by the {111} A planes to the height of the buffer layer. One depression produces two smaller symmetrical depressions. As a result, these depressions permeate the entire grown structure. This leads to structural defects in the epitaxial layers and short circuits of *p-n* transitions. Such heterostructures lead to a high rate of rejection in the manufacture of semiconductor devices and non-reproducibility of electrophysical parameters over the area of the epitaxial plate.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors:

Mikhail G. Vasil'ev, DSc in Technical Sciences, Professor, Head of the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation, e-mail: mgvas@igic.ras.ru. ORCID iD: https://orcid.org/0000-0002-4279-1707.

Anton M. Vasil'ev, Researcher Fellow, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation e-mail: toto71@bk.ru. ORCID iD: https://orcid.org/0000-0002-9901-5856.

Alexander D. Izotov, DSc in Chemistry, Corresponding Member of the Russian Academy of Sciences, Chief Researcher of the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation, e-mail: izotov@igic.ras.ru. ORCID iD: https://orcid.org/0000-0002-4639-3415.

Yuriy O. Kostin, PhD in Technical Science, Senior Researcher, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation, e-mail: temptelam@yandex.ru. ORCID iD: https://orcid.org/0000-0001-8172-3988.

Alexey A. Shelyakin, PhD in Technical Science, Senior Researcher of the Laboratory of Semiconductor and Dielectric Materials, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation, e-mail: aleksscheliakin@gmail.com. ORCID iD: https://orcid.org/0000-0003-0028-005X.

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