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The Preparation and Properties of Indium Phosphide

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The present review examines recent work on the synthesis of polycrystalline specimens of indium phosphide and the growth of single crystals of this compound for the modern electronics industry. The synthesis of polycrystalline indium phosphide by different methods is examined. Particular attention has been paid to work on the preparation of highly pure material and the growth of single crystals with a low concentration of dislocations and single crystals oriented along ⟨100⟩.
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I. INTRODUCTION

In recent years, in the development of work in optoelectronics (the use of optical and electronic effects in semiconductors to create instruments and information systems of fundamentally new types) and SHF (super-high-frequency) technology, there has been a marked increase in interest in single crystals of indium phosphide. Indium phosphide now occupies third place in the world after silicon and gallium arsenide in importance for application in special instruments. Non-doped single crystals of indium phosphide are used as supports in the manufacture of instruments in SHF technology. The main requirement in this material is a low concentration of impurities, which affect the parameters of the instruments, and a low density of dislocations. Field transistors are produced on supports of single crystals of semi-insulating indium phosphide with a high specific resistance ($\rho > 10^7$ Ω.cm). The main application of single crystals of indium phosphide, however, is in optoelectronics, for producing radiation sources and receivers operating in the wavelength range 1.0–1.6 μm.

II. THE PREPARATION OF HIGHLY PURE INDIUM PHOSPHIDE CRYSTALS

Non-doped polycrystalline indium phosphide is obtained chiefly by the following methods: horizontal directed crystallisation, horizontal zone fusion, crystallisation of melts with non-stoichiometric composition in a temperature gradient (so-called "synthesis with diffusion through a melt"), and synthesis in quasi-hermetic reactors. Polycrystalline indium phosphide is used in liquid-phase epitaxy and as starting material for growing single crystals.

1. Horizontal Directed Crystallisation (HDC)

The synthesis of indium phosphide by HDC has been carried out in an autoclave.[1,2] Boats of pyrolytic boron nitride (PBN) or quartz containing indium and red phosphorus were placed in a sealed quartz ampoule (reactor). The synthesis was carried out at the melting point of the indium–indium phosphide melt (1070 °C) at the equilibrium vapour pressure of phosphorus, 27.5 atm (the temperature of the section of the ampoule containing phosphorus was ~600 °C). The boat containing indium was heated at a rate of 20–35 K h^{-1}, and that containing phosphorus at a rate of 10 K h^{-1}. The pressure of inert gas in the autoclave was raised simultaneously. The low heating rates prevented rupture of the ampoule with increase in the phosphorus vapour pressure. When the reaction was complete, the temperature of the hot zone (the zone containing the indium–indium phosphide melt) was lowered at a rate ensuring crystallisation (0.2–0.5 cm h^{-1}). Indium phosphide ingots with a mass of 110 g were obtained after 170 h.[2] The concentration of principal current carriers in these ingots was $n = (2–5) \times 10^{15}$ cm^{-3} (300 K).

HDC has been used[3] to obtain polycrystalline indium phosphide ingots with a mass of 1100 g. The synthesis was carried out in an autoclave, in a quartz ampoule with diameter 34–38 mm and length 300 mm. This gave a product with $n = (5–50) \times 10^{15}$ cm^{-3} and a mobility of principal charge carriers $u = (1.5–2.5) \times 10^4$ cm^2 V^{-1} s^{-1} (77 K). The concentration of silicon did not exceed $(2–3) \times 10^{-5}$ at.% or $(4–6) \times 10^{15}$ atom cm^{-3}. The authors cited consider that the main source of silicon in the indium phosphide is impurities in the original indium.

In Ref.4, the purity of indium phosphide was increased by heating the indium at 700 °C successively (100 h) in a stream of moist hydrogen and in a vacuum at 10^{-7} mmHg, and heating the phosphorus in a vacuum at 300–335 °C for 24 h. The quartz parts of the reaction vessel, after etching, were heated in a vacuum at 1000 °C before assembling the reaction vessel. The PBN boats were also specially treated. Under these conditions, ingots of polycrystalline indium phosphide with $n = 10^{15}$ cm^{-3} and $u = (3–4) \times 10^4$ cm^2 V^{-1} s^{-1} (77 K) were obtained.

A significant increase in the purity of polycrystalline indium phosphide is achieved by recrystallising its non-stoichiometric melts. In Ref.5, indium phosphide synthesised at the equilibrium vapour pressure of phosphorus had $n = 3.50 \times 10^{15}$ cm^{-3} and $u = 2.52 \times 10^4$ cm^2 V^{-1} s^{-1} (77 K), whereas the material obtained at a lower phosphorus vapour pressure above the melt (lower than 10 atm) had $n = 3.16 \times 10^{15}$ cm^{-3} and $u = 3.89 \times 10^4$ cm^2 V^{-1} s^{-1}. The crystallisation of melts with non-stoichiometric composition, however, requires a decrease in the crystallisation rate (12 mm d^{-1}).

To increase the purity of indium phosphide synthesised by HDC, indium(III) oxide was added to the reaction vessel to an atomic fraction of 10^{-4}–10^{-5}. The doping with oxygen was carried out for two sets of growth conditions, with one high-temperature zone (1080 °C) in an ampoule with length 100 mm, and with two zones (1080 °C and 630 °C) in an ampoule of length 300 mm.[6]

Measurement of the electrical parameters by the Hall effect method showed a decrease in the concentration of charge carriers and an increase in their mobility compared with specimens not doped with oxygen only when the doped indium phosphide was grown in a single temperature zone: the values were $(1.5–7) \times 10^{15}$ cm^{-3} and $(2–3.3) \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K) respectively. The influence of oxygen under these conditions is due to the decrease in the concentration of the silicon fine donor impurity in the indium phosphide crystal.

To increase the productivity of the synthesis of indium phosphide by HDC and to prevent possible rupture of the sealed quartz reactors, they are fitted with a quartz bellows, which connects the quartz rod to the pressure measuring device in the autoclave.[7] The signal from the measuring device is passed to a system which equalises the pressure in the reactor and the autoclave (Fig.1). In an autoclave fitted with this system it is possible to synthesise in 1 h 2 kg of indium phosphide with parameters $n = 1.5 \times 10^{16}$ cm^{-3} and $u = 1.5 \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K).

In work at one of the leading firms producing semiconducting compounds, Metal Chemical Products (England),[8] the pressure in the ampoule and in the autoclave is controlled using a quartz reaction vessel, in the end face of which there is sealed a corrugated quartz diaphragm, connecting the rod to the pressure measuring device. The signal from the measuring device operates solenoid valves to supply gas to the autoclave or to release the pressure when the phosphorus vapour pressure in the reactor increases. This system gives a differential pressure difference of 0.25–0.5 atm, depending on the sensitivity of the diaphragm.

The conditions for obtaining ingots of indium phosphide with improved parameters were investigated in the same study: the main requirement was additional treatment of the starting materials. Indium was heated in a vacuum at 900 °C (12 h). The time taken to synthesise a melt with a mass of 2 kg in quartz boats at a phosphorus vapour pressure of 24.5–30 atm was 20 h, and the crystallisation rate was 10–20 mm h^{-1}. The polycrystalline indium phosphide ingots obtained under these conditions had $n = 5 \times 10^{5}$ cm^{-3} and $u = (2–4) \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K); the silicon concentration was 2×10^{-5} mass % or 2×10^{15} atom cm^{-3}.

2. Horizontal Zone Fusion (HZF)

The HZF directed crystallisation method is widely used by Western European firms to obtain polycrystalline highly pure indium phosphide. The product has been synthesised in an autoclave, in a sealed quartz ampoule.[9,10] The temperature of the molten zone was 1100 °C, and the phosphorus vapour pressure 27.5 atm. The ampoule was moved relative to the inductor at a rate of 6 cm h^{-1}, and after 6 h, 1.3 kg of polycrystalline indium phosphide was obtained:[10] $n = (5–10) \times 10^{15}$ cm^{-3}, $u = 3700–4700$ cm^2 V^{-1} s^{-1} (300 K). The concentration of silicon in the indium phosphide ingots obtained did not exceed 10^{16} atm cm^{-3}. The main source of silicon in the product was the impurities in the original indium.

With increase in the temperature of the molten zone from 1050 °C to 1180 °C, the concentration of principal charge carriers increased approximately 100-fold, due to an increase in the silicon concentration.[11] The authors cited point out that decrease in the phosphorus vapour pressure in the ampoule to 2 atm makes possible an approximately five-fold decrease in the concentration of principal charge carriers. To increase the purity of the polycrystalline specimens obtained, the original indium was heated beforehand in a vacuum (3 h) at 450–950 °C. The temperature conditions of the preliminary vacuum treatment of the original indium had the greatest influence on the purity of the synthesised indium phosphide. In the opinion of the authors cited, the concentration of silicon in polycrystalline indium phosphide is lower if the original metallic indium contains oxides, which decompose in a vacuum at >800 °C. Increase in the indium heating temperature from 700 °C to 800 °C led to a sharp increase in the concentration of both the principal charge

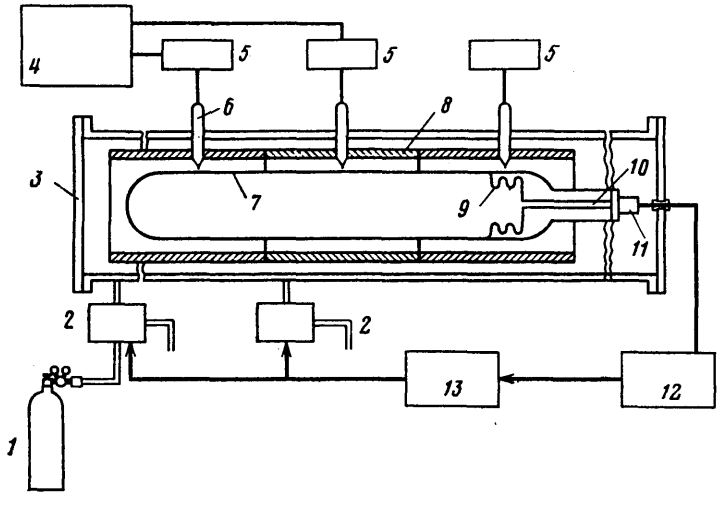


Figure 1. Block diagram of the high-pressure apparatus for synthesising polycrystalline indium phosphide ingots, fitted with a system balancing the pressure in the reactor and the autoclave: *1*) cyclinder of inert gas, *2*) high-pressure valve, with electric drive, *3*) autoclave, *4*) potentiometer, *5*) blocks of high-precision temperature regulators (HTR), *6*) thermocouple, *7*) reactor containing boat with indium and red phosphorus (not shown in the diagram), *8*) heater, *9*) quartz bellows, *10*) rod, *11*) high-pressure measuring device, *12*) amplifier, *13*) automatic regulator controlling the operation of the high-pressure valve.[7]

carriers and silicon in the polycrystalline indium phosphide obtained. The authors cited consider that the reaction of indium oxides with phosphorus vapour gives phosphorus(V) oxide, whose partial pressure in the ampoule increases, and the equilibrium[12]

$$10SiO_2(solid) + P_4(gas) \rightleftarrows 10SiO(gas) + P_4O_{10}(gas)$$

is displaced to the left, leading to contamination of indium phosphide by silicon from the quartz boat. Highly pure polycrystalline indium phosphide with $n = 3.2 \times 10^{15}$ cm^{-3} and $u = 3.7 \times 10^4$ cm^2 V^{-1} s^{-1} (77 K) has been obtained.[11]

3. Crystallisation of a Melt with Non-stoichiometric Composition in a Temperature Gradient

This method of synthesising indium phosphide, called "synthesis with diffusion through a melt", is used mainly by Japanese firms. Recently, however, it has attracted interest from Western European research workers. The chief advantages are the simplicity of the equipment, which does not require the use of autoclave assemblies, and the high purity, compared with HDC and HZF, of the material obtained, resulting from the use of low synthesis temperatures (750–910 °C).

In Ref.13, indium phosphide was synthesised in a sealed quartz ampoule, placed in a two-zone furnace. The starting materials were red phosphorus (5 g) and indium (37.5 g), heated beforehand in a stream of hydrogen at 850 °C for 72 h. A quartz crucible containing red phosphorus was placed in the upper part of the ampoule, and indium in the lower part. The synthesis was carried out at 850 °C and a phosphorus vapour pressure of 0.8 atm (temperature of the upper part of the ampoule 400 °C). The temperature gradient required to crystallise indium phosphide from the saturated solution was created along the height of the melt. Under these conditions the synthesis was continued for 10 d to give a single-crystal ingot of indium phosphide with length and diameter 15 mm, mass 5.5 g, density of dislocations $N_d = 10^2$ cm^{-2}. When the process was complete, the indium was found to contain thin plates of indium phosphide with dimensions of several millimetres. The growth rate was 0.15 cm d^{-1}. The indium phosphide obtained under these conditions had $n = 2.3 \times 10^{14}$ cm^{-3} and $u = 5.02 \times 10^4$ cm^2 V^{-1} s^{-1} (77 K).

To increase the purity of the product, indium was heated beforehand at 900 °C for 6 h; the red phosphorus was also heated beforehand (120 °C for 6 h). At a melt temperature of 910 °C and a temperature gradient in the melt of 20 K cm^{-1}, the indium phosphide obtained had $n = 6.4 \times 10^{14}$ cm^{-3} (300 K) and $u = 7.91 \times 10^4$ cm^2 V^{-1} s^{-1} (77 K).[14] Later, the same authors reported the preparation of indium phosphide with $n = 5.9 \times 10^{14}$ cm^{-3} (300 K) and $u = 9.67 \times 10^4$ cm^2 V^{-1} s^{-1}.[15] The principal donor impurities in the indium phosphide are silicon and sulphur.

4. Synthesis of Indium Phosphide in Quasi-hermetic Reactors

The most productive method of obtaining polycrystalline indium phosphide is by synthesis in quasi-hermetic reactors, in an autoclave assembly. Fig.2 gives a diagram of the apparatus for synthesising polycrystalline indium phosphide ingots.[16] A hydraulic seal was used to connect the separate parts of the reactor, that is the quartz part containing red phosphorus and the graphite part containing the quartz crucible with indium.

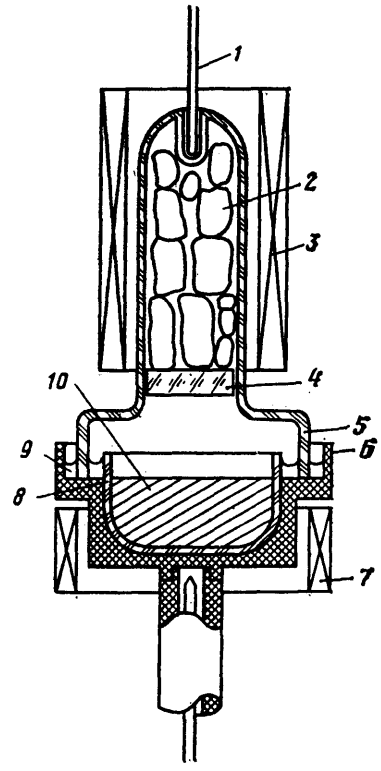


Figure 2. Diagram of the quasi-hermetic apparatus for synthesising indium phosphide by the reaction of phosphorus vapour with molten indium: *1*) thermocouple, *2*) phosphorus, *3*) electrical resistance heater, *4*) quartz plate, *5*) quartz reactor, *6*) graphite support, *7*) crucible heater, *8*) quartz crucible, *9*) channel of hydraulic seal, filled with indium, *10*) molten indium.[16]

A weighed specimen of indium (from one to several kilograms) was placed in the crucible. The corresponding stoichiometric quantity of red phosphorus, together with the calculated excess to fill the free volume of the reactor and to compensate the loss through the hydraulic seal (several percent of the total quantity) was placed in the quartz part of the reactor. The high-pressure chamber was evacuated, and then filled with an inert gas at a pressure such that after the heater was switched on, the working pressure in it was 60 to 70 atm. The red phosphorus was then heated to a temperature ensuring that the phosphorus vapour pressure created in the reactor was greater than the equilibrium vapour pressure over the molten compound with the stoichiometric composition (25 atm), and the crucible with the molten indium was heated to 1060 °C, and kept until the synthesis was complete. The temperature of the melt in the crucible was then lowered slowly to give a polycrystalline ingot of the compound. The material had electron conductivity and $n = (1–2) \times 10^{16}$ cm^{-3} and $u = 3500–4500$ cm^2 V^{-1} s^{-1} (300 K).[16]

The time required to carry out the synthesis in a quasi-hermetic reactor by the HZF and HDC methods was calculated from the Nernst equation:[17]

$$\tau = \frac{-2.303 \cdot V \cdot \lg[(C_e - C_\tau)/(C_e - C_0)]}{F \cdot \alpha}$$

where α is the reaction coefficient (the rate constant of the first-order reaction taking place on the melt surface), cm s^{-1}; F the surface area of the melt, cm^2; C_e and C_0 the equilibrium (for the given temperature of the melt and vapour pressure of the volatile component) and initial concentrations of the volatile element in the melt, g cm^{-3} or atom cm^{-3}; V the volume of the molten non-volatile element, cm^3; and C_τ the concentration of the volatile element in the melt at moment of time τ, g cm^{-3} or atom cm^{-3}.

Fairly full thermochemical parameters of the synthesis of indium phosphide are given in Ref.18.

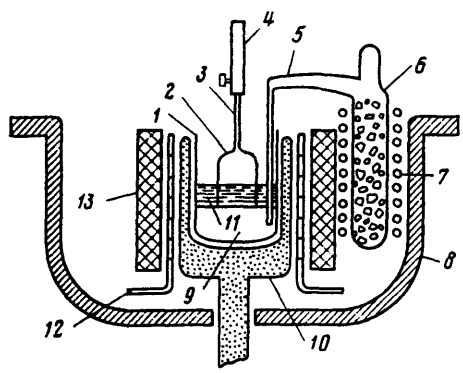


Figure 3. Diagram of the thermal unit of the high-pressure apparatus for obtaining indium phosphide crystals by the combined method (synthesis followed by crystal growth): *1*) crucible, *2*) crystal, *3*) seed, *4*) seed holder, *5*) tube for supplying phosphorus vapour from the reservoir, *6*,*7*) electrical resistance heater, *8*) autoclave body, *9*) melt, *10*) graphite support, *11*) layer of flux (B_2O_3), *12*) graphite electrical heater, *13*) heat reflecting screen.[19]

5. Combined Process

To increase the purity of polycrystalline and single-crystal indium phosphide, a combined process has been used: the synthesis was carried out directly in the apparatus used to grow single crystals; phosphorus vapour (30.6 atm) was supplied to molten indium under a layer of molten boric oxide (Fig.3).[19] The synthesis was carried out at the temperature of the indium–indium phosphide melt (1100 °C) for 1.5 h. This gave indium phosphide crystals with $n = (1.85–2.57) \times 10^{15}$ cm^{-3} and $u = (3.03–3.18) \times 10^4$ cm^2 V^{-1} s^{-1} (77 K). The parameters of indium phosphide crystals obtained in quartz and PBN crucibles, and the silicon concentrations [$(0.3–0.5) \times 10^{-4}$ mass % or $(6–10) \times 10^{15}$ atom cm^{-3}], differed little. Approximately the same quantity of silicon is present in polycrystalline indium phosphide synthesised by other methods.

Examination of the methods for synthesising polycrystalline indium phosphide leads to the following conclusions.

1. To obtain weakly-doped single crystals with a concentration of charge carriers lower than 10^{17} cm^{-3}, the most suitable method is horizontal zone fusion. When systems controlling the pressure in the hermetic reactor and the gas pressure in the autoclave are developed, this method will satisfy all the requirements of ecological purity and safe operation.
2. Material to be used to grow highly-doped indium phosphide single crystals is best synthesised in a quasi-hermetic reactor. This method has a high productivity, and the cost of the final product is low.
3. The liquid-phase epitaxy of layers of indium phosphide and solid solutions based on it requires a relatively small quantity of highly pure polycrystalline indium phosphide. This material can be obtained by different versions of the directed crystallisation of indium–phosphorus melts with non-stoichiometric composition. Crystallisation at temperatures not exceeding 900 °C ensures minimum contamination of the final product by the reaction of the melt with the material of the container.

III. THE GROWTH OF SINGLE CRYSTALS OF INDIUM PHOSPHIDE BY LIQUID HERMETIC SEALING OF THE MELT

1. Apparatus and Conditions for Growing Single Crystals of Indium Phosphide without Twins

One of the most widely encountered versions of the Czochralski method[18] is the so-called method of liquid hermetic sealing of the melt with a flux (LHM), widely used to grow single crystals of semiconducting compounds which may decompose. Single crystals of indium phosphide are grown by LHM in autoclave assemblies using resistance or high-frequency heating. The process is carried out in an inert gas (nitrogen or argon) atmosphere at a pressure of 30–60 atm. Boric oxide is used as flux.

Workers at the Nippon Telegraph and Telephone Public Corporation (Japan) have grown single crystals of indium phosphide in MSR6R high-pressure assemblies (Metals Research, England) using resistance heating. The temperature of the melt in the quartz crucible was kept constant to within ±0.1 K using a thermocouple placed at the bottom of the crucible. The starting material, synthesised by HZF, with $n = (8–40) \times 10^{15}$ cm^{-3} (300 K), was placed in crucibles with diameter 50 mm or 100 mm (95 g and 300 g respectively). The thickness of the layer of flux varied from 6 mm to 24 mm.[20–22] Single crystals of indium phosphide were grown in the crystallographic direction <111>; the seed was raised at a rate of 10–12 mm h^{-1}. The crucible and the seed were rotated in the same direction at rates of 5 r.p.m. and 3 r.p.m. respectively. A nitrogen pressure of 35 atm was maintained in the chamber. This gave non-doped single crystals of indium phosphide with diameter 25 mm, with $n = 4.8 \times 10^{15}$ cm^{-3} and $u = 2.68 \times 10^4$ cm^2 V^{-1} s^{-1} (77 K).[22]

Specialists at Bell (USA) used an autoclave assembly with induction heating (450 kHz) to grow single crystals of indium phosphide. The original polycrystalline material with $n = (2–5) \times 10^{15}$ cm^{-3} (77 K) was synthesised by HDC. The single crystals were grown in the crystallographic direction <111> under the following conditions: nitrogen pressure in the compartment 38 atm; seed raised at a rate of 13–17 mm h^{-1}; rate of rotation 20–30 r.p.m.; thickness of layer of flux 5 mm (15 g boric oxide). The crucibles, with diameter

38 mm, were made of quartz or PBN. The non-doped single crystals of indium phosphide with diameter 30 mm and 80 mm had $N_d = 7 \times 10^3 - 5 \times 10^5$ cm^{-2}.[1,2,23]

Single crystals of indium phosphide with large diameter (greater than 40 mm) have been grown in MSR6R and Melbourn (England) assemblies. In the first assembly, crystals were grown in the crystallographic directions <111> and <100> in quartz or PBN crucibles with height and diameter 100 mm, containing the original polycrystalline indium phosphide (1 kg). Crystallisation at a rate of 9 mm h^{-1} gave non-doped single crystals of indium phosphide with diameter 45–60 mm, mass 800 g, and $N_d = (1-10) \times 10^4$ cm^{-2}.[10]

Single crystals of indium phosphide with diameter 80 mm and mass 3 kg were grown in the Melbourn apparatus from crucibles with height and diameter 150 mm containing the original polycrystalline indium phosphide (3.5 kg). The density of dislocations in these crystals was $(3-8) \times 10^4$ cm^{-2}.[10]

The main technical difficulty in the growth of single crystals of indium phosphide by LHM is twinning of the crystals in the initial stage of growth. When the process is carried out in the crystallographic direction <111>, to prevent twinning, the crystal is grown from a seed to a constant diameter at an angle ≤19° 68′ relative to the growth axis.[1,2,20–28] These growth conditions prevent twinning along the (111) planes (Fig. 4), which lie at an angle of 70° 32′ to the direction of growth.

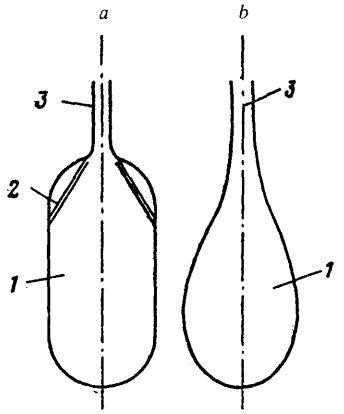


Figure 4. Profile of single crystals of indium phosphide grown from the seed to the nominal diameter in the <111> direction at an angle greater than (a) and less than (b) 19° 68′: *1*) single crystal, *2*) twinning planes, *3*) seed.[2]

When single crystals of indium phosphide are grown in the crystallographic direction <100>, the probability of twinning is reduced considerably if the crystal is grown from the seed to a constant diameter without vertical movement of the seed (angle of growth relative to the growth axis ~90°).[10]

During growth, twins may be produced in the crystal as a result of the introduction into the crystallisation front of foreign inclusions (oxides, gas bubbles, etc.) present on the surface of the molten indium phosphide. Special preparation of the flux to obtain a pure melt (without bubbles) has been carried out in a platinum crucible at 1000 °C in a vacuum for 24 h.[1,29] Before use, the boric oxide was kept in a quartz ampoule in a vacuum at 5×10^{-6} mmHg. The residual bubbles were removed from the flux by rotating the seed at an increased rate (greater than 20 r.p.m.).

The thermal decomposition of the indium phosphide single crystal after its removal from under the layer of flux may lead to the flow of the free indium liberated along the crystal to the crystallisation front.[21] Thus to prevent decomposition of the surface of the single crystal of indium phosphide it is necessary, after removing it from under the layer of flux, to cover it with a thin layer of flux. To achieve this, the temperature of the flux must be kept at ~550 °C.

The probability of twinning in single crystals of indium phosphide is reduced by decreasing the thermoelastic stresses produced during growth, and also by doping the indium phosphide with strengthening impurities such as zinc and sulphur (not more than 10^{18} atom cm^{-3} [29] or antimony $(1.7-7.2) \times 10^{-3}$ mass %.[30]

2. Preparation of Highly Pure Non-Doped Single Crystals of Indium Phosphide

During the growth of single crystals of indium phosphide by LHM, the product is contaminated by impurities entrained by the faces of the granules of the original polycrystalline material and impurities present in the flux (boric oxide).[29] Another source of contamination is the volatilisation of impurities from the graphite screens.[15] Thus when screens previously heated in a vacuum at 1300 °C were used, the concentration of principal charge carriers in indium phosphide was lowered by a factor of approximately two. Silicon is the chief background impurity, and it produces marked changes in the characteristics of instruments based on indium phosphide:[15,21,22,29] the concentration of silicon is $(6-16) \times 10^{15}$ atom cm^{-3}.[22,31]

During the growth of single crystals in a quartz crucible, silicon is transferred to the melt as a result of a reaction between indium phosphide and silicon(IV) oxide.[15] To decrease the concentration of silicon in the melt and the crystal, PBN crucibles are used. Another source of silicon is low-melting borosilicate glass, a thin layer of which is formed on the walls of the quartz crucible.[32] Since the chemical bond between silicon and oxygen is weaker in this layer, the transfer of silicon to the indium phosphide melt is facilitated. An increase in the concentration of silicon in the flux (boric oxide) has been detected after indium phosphide crystals have been grown in a quartz crucible. In the flux situated at the centre of the crucible, the silicon concentration was 62 times that in the original boric oxide, and at the wall of the quartz crucible the corresponding factor was 2200. When PBN crucibles were used, the concentration of silicon in the flux after the growth of indium phosphide crystals remained unchanged. This confirms that PBN crucibles must be used to grow highly pure indium phosphide crystals by LHM.

A change in the nature of the distribution of silicon in a crystal grown in a PBN crucible has been detected:[32] the effective distribution coefficient increased to $k > 1$. This change is apparently due to the extraction of silicon from the indium phosphide melt by the boron(III) oxide flux.

It should however be noted that the use of PBN crucibles leads to appreciable contamination of indium phosphide by boron, and in some cases to the appearance of traces of a second phase during growth, as a result of the reaction of boric oxide with PBN.[9]

To increase the purity of indium phosphide, melts with non-stoichiometric composition have been crystallised;[33] the original polycrystalline material, synthesised by HZF in a high-pressure assembly, was crystallised (at a rate of 6 mm h^{-1}) by LHM with the addition of 10 mass % and 20 mass % indium. The addition of 20 mass % indium gives best results. In the first case (10 mass % indium), original material with $n = 4 \times 10^{15}$ cm^{-3} and $u = 1.815 \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K) gave an indium phosphide crystal with $n = 3.24 \times 10^{15}$ cm^{-3} and $u = 3.015 \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K). In the second case (20 mass % indium), a material with $n = 9.02 \times 10^{15}$ cm^{-3} and $u = 7.5 \times 10^{3}$ cm^2 V^{-1} s^{-1} gave a crystal with $n = 9.36 \times 10^{15}$ cm^{-3} and $u = 1.517 \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K). The concentration of silicon in the best indium phosphide specimens obtained by LHM was (1.0–1.5) $\times 10^{-6}$ at.% or (2–3) $\times 10^{14}$ atom cm^{-3}.

3. Production of Doped Single Crystals of Indium Phosphide

To obtain single crystals with electron and hole conductivity and a high concentration of principal charge carriers, used to produce optoelectronic instruments, indium phosphide is doped with the donor impurities tin and sulphur and the acceptor impurity zinc (see Table).

Parameters of single crystals of indium phosphide with diameter 40–55 mm, produced by Sumimoto (Japan) in 1982.[34]

Dopant	Electrophysical parameters at 300 K			Dislocation density, cm^{-2} (not more than)
	concentration of principal charge carriers, cm^{-3}	mobility of principal charge carriers, $cm^2V^{-1}s^{-1}$	specific resistance, Ω.cm	
Tin	5×10^{17}–6×10^{18}	1200–2500	5×10^{-4}–6×10^{-3}	5×10^{4}
Sulphur	not less than 2×10^{18}	800–1800	not more than 1.8×10^{-3}	5×10^{3}
Zinc	not less than 2×10^{18}	35–60	not more than 5×10^{-2}	5×10^{3}
Zinc	1×10^{15}–5×10^{16}	80–150	1.5–80	5×10^{4}

In the USSR, single crystals of indium phosphide doped with tellurium are also used (diameter 20–40 mm; length not less than 25 mm), with $n = (5–500) \times 10^{16}$ cm^{-3}, $u = (1$ to $2.5) \times 10^{3}$ cm^2 V^{-1} s^{-1} (300 K), and $N_d < 5 \times 10^{4}$ cm^{-2}.

Doping indium phosphide with iron and chromium impurities gives single crystals with a high specific resistance. The specific resistance (ρ) of single crystals of indium phosphide doped with chromium does not exceed 5×10^{3} Ω.cm,[35] whereas doping with iron gives a material with $\rho > 10^{7}$ Ω.cm.[2,15,19,35–38] Thus iron is usually employed to obtain semi-insulating indium phosphide.

Single crystals of semi-insulating indium phosphide have been grown by LHM in the crystallographic directions <111> and <100>. The starting material was indium phopshide with maximum purity ($n = 5 \times 10^{15}$ cm^{-3} and $u = (2.5–3.5) \times 10^{4}$ cm^2 V^{-1} s^{-1}),[15,34] giving crystals with $\rho > 10^{7}$ Ω.cm with a low concentration of iron in the melt (0.002–0.04 mass %).

Fig.5 gives the dependence of the specific resistance of indium phosphide on the proportion of crystallised melt for different concentrations of iron in it. To obtain crystals with $\rho > 10^{7}$ Ω.cm along the entire length it is evidently necessary to add 0.02–0.04 mass % iron to the melt. With increase in the concentration of iron in the melt to 0.1 mass %, the production of single crystals is made difficult by twinning as a result of non-metal inclusions on the surface of the melt.[15] To ensure thermal stability of the material during annealing after iron implantation, it is necessary to lower the iron concentration to 0.022 mass %. If the iron concentration in the crystal exceeds 8.8×10^{15} atom cm^{-3}, then the specific resistance after annealing the indium phosphide specimens at 750 °C is lowered.[36]

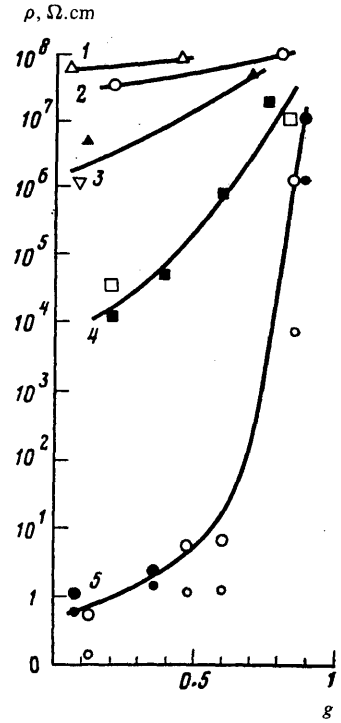


Figure 5. Distribution of the specific resistance along the length of a single crystal (*g*) of semi-insulating indium phosphide doped with iron (mass % in the melt): *1*) 0.15; *2*) 0.04; *3*) 0.02; *4*) 0.01; *5*) 0.005.[15]

Single crystals of semi-insulating indium phosphide with diameter 45–55 mm have been grown in the crystallographic direction <100> in autoclave assemblies under a nitrogen pressure of 50 atm (seed raised at a rate of 7–10 mm h^{-1}, rate of rotation of the seed and the crucible 7–15 r.p.m.) from under a layer of flux with thickness 18–20 mm. The temperature gradient in the region of the flux–melt boundary was about 100 K cm^{-1}. The dislocation density was (2–4) $\times 10^{4}$ cm^{-2} in the initial section of the ingots, and (6–15) $\times 10^{4}$ cm^{-2} in the final section.[36]

Polycrystalline indium phosphide with $n = (2–4) \times 10^{15}$ cm^{-3} and $u = (2.5–3.0) \times 10^{4}$ cm^2 V^{-1} s^{-1} (77 K) has been used[26] to obtain cobalt-doped (2×10^{-3} mass %) semi-insulating indium phosphide with $\rho > 10^{7}$ Ω.cm. The effective distribution coefficient of cobalt in the indium phosphide was 4×10^{-5}, and the concentration of cobalt in the initial section of the crystal was 4×10^{15} atom cm^{-3}. At this concentration of cobalt in the crystals, however, there was considerable separation of secondary phases—cobalt(III) phosphide and

phases of indefinite structure containing 70 mass % phosphorus and 30 mass % cobalt.[26,39] The separation of secondary phases began approximately half way along the length of the ingot.

4. Preparation of Low-Dislocation and Dislocation-Free Single Crystals of Indium Phosphide

To obtain low-dislocation and dislocation-free semiconductor single crystals, the thermoelastic stresses τ_{te} produced in the crystal during growth and cooling should not exceed the critical stresses of dislocation formation τ_{cr}. The values of τ_{te} can be lowered, and the minimum density of dislocations in single crystals of indium phosphide obtained, by growing under temperature conditions ensuring the minimum axial and radial temperature gradients.

Dislocation-free non-doped single crystals of indium phosphide with diameter not greater than 15 mm have been obtained by growing a thin "neck" on the seed.[20-22] This method made it possible to obtain dislocation-free single crystals on seeds with a dislocation density of 10^5 cm^{-2}. After the annihilation of the dislocations in the "neck", new dislocations were produced in the crystal when the diameter exceeded the critical value, which depends on the axial and radial gradients. Small temperature gradients $\partial T/\partial x$ were achieved by increasing the thickness of the layer of boric oxide (δ). Thus for δ = 6 mm, $\partial T/\partial x$ = 175 K cm^{-1}, which ensured the production of non-doped dislocation-free single crystals of indium phosphide with diameter 8 mm. At δ = 13 mm and $\partial T/\partial x$ = 55 K cm^{-1}, the diameter of the dislocation-free crystals increased to 15 mm.[21]

A theoretical calculation[21] has shown that to obtain non-doped dislocation-free single crystals of indium phosphide with diameter 25 mm it is necessary to decrease the temperature gradient to 20 K cm^{-1}, or to 5 K cm^{-1} for a diameter of 50 mm. It is practically impossible, however, to achieve these gradients, either by increasing the thickness of the layer of flux or by other methods. Thus the maximum diameter of non-doped dislocation-free single crystals of indium phosphide is not greater than 15 mm. With increase in the diameter of the crystal, dislocations are generated at the periphery of the ingot and multiply into the depth of the crystal.

The dislocation density in indium phosphide crystals with a large diameter (>40 mm) during growth has been reduced using a system for automatically controlling the diameter by weighing the crucible.[15,24-27,36] The stresses in the crystal after growth were removed by annealing at a high inert-gas pressure (~38 atm).[2,23] This decreased the dislocation density by a factor of approximately ten.[2]

A more promising method for decreasing the dislocation density in indium phosphide is by increasing τ_{cr} by doping with strengthening impurities. Impurity atoms with dimensions smaller than those of the atoms of the components of the semiconducting compound being replaced lower considerably the dislocation density in single crystals of these compounds. The same applies to a lesser extent to large atoms (Fig.6).[40] Zinc, sulphur, and germanium are used as impurities of this kind.[24,41,42]

Calculation shows that the maximum thermoelastic stresses produced during the growth of single crystals of indium phosphide correspond to 800 °C. The difference in the values of τ_{cr} for non-doped single crystals and single crystals doped with zinc (2×10^{18} atom cm^{-3}) is extremely large (Fig.7). This calculation confirms the temperature range of dislocation formation obtained by analysing the characteristic features of the dislocation structure.[42]

Increase in the concentration of zinc to 10^{19} atom cm^{-3} and of sulphur to 10^{19} atom cm^{-3} has been used to obtain dislocation-free single crystals of indium phosphide with a diameter of not more than 30 mm.[41] Combined doping with zinc and sulphur to a total concentration of 2×10^{19} atom cm^{-3} made it possible to lower the dislocation density in single crystals of indium phosphide with diameter 30 mm to 10^2–10^3 cm^{-2}.[43]

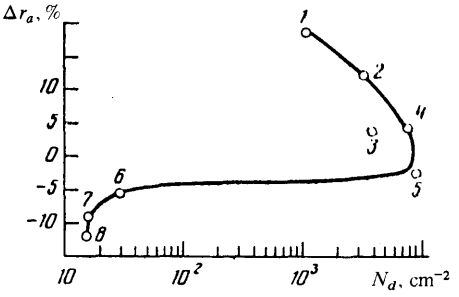


Figure 6. Influence of the difference between the tetrahedral radii of the impurity and the atom of the compound being replaced (Δr_a) on the dislocation density (N_d) in single crystals of indium phosphide and gallium arsenide doped with various elements: *1*) InP(Te); *2*) GaAs(Te); *3*) InP(Se); *4*) GaAs(Zn); *5*) InP(Sn); *6*) InP(S); *7*) InP(Zn); *8*) GaAs(S).[40]

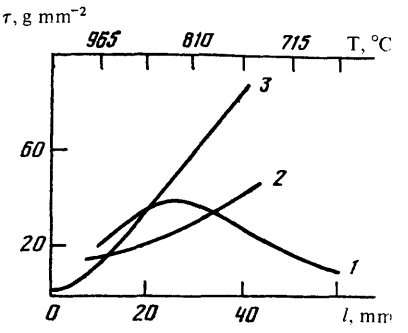


Figure 7. Comparison of the thermoelectric stresses (τ_{te}) along the axis of indium phosphide crystals and the critical stresses of dislocation formation (τ_{cr}) at corresponding temperatures at a distance l from the crystallisation front: *1*) τ_{te}; *2*) τ_{cr} for non-doped indium phosphide; *3*) τ_{cr} for indium phosphide doped with zinc ($p = 2 \times 10^{18}$ cm^{-3}).[42]

Single crystals of indium phosphide with diameter 26 mm, doped with germanium (1.5×10^{17}–1.6×10^{19} atom cm^{-3}), have been grown in the crystallographic direction <111>.[24] Dislocation-free crystals were obtained with $n = 1.1 \times 10^{19}$ cm^{-3} and $n = 1.6 \times 10^{19}$ cm^{-3}; in other cases the dislocation density was $(2.2–5) \times 10^4$ cm^{-2}. Decrease in the dislocation

density began at a germanium concentration greater than 7×10^{18} atom cm^{-3}. A disadvantage of doping with germanium is that large defects (>50 nm) of unusual shape (oval), lying on dislocation lines, appear in the indium phosphide structure.[25,27,37,42,44] Thus in practice, doping with zinc and sulphur is used to decrease the dislocation density in indium phosphide. In Japan, low-dislocation single crystals of indium phosphide with $N_d < 10^2$ cm^{-2} and diameter 20–30 mm have been obtained on the industrial scale.

Attempts to dope indium phosphide with isovalent impurities, which have been used successfully to dope gallium arsenide (antimony, arsenic, etc.), have not yet given satisfactory results.[45]

5. Some Characteristic Features of the Dislocation Structure of Single Crystals of Indium Phosphide

Selective chemical etching of indium phosphide specimens has revealed several types of etch pit, corresponding to linear dislocations, dislocation loops, and dislocation clusters. In addition, in some specimens, *s*-shaped etch pits of non-dislocation character (fine-point background) have been detected. This background has been observed in single crystals of indium phosphide doped with tin (2×10^{18} atom cm^{-3}; density of *s*-shaped etch pits 6×10^4 cm^{-2}) and sulphur (10^{19} atom cm^{-3}; density of *s*-shaped etch pits 2×10^3 cm^{-2}).[41]

Structural defects of the dislocation cluster type have been detected by selective chemical etching and X-ray topography both in non-doped indium phosphide single crystals and in specimens doped with germanium, tin, iron, and selenium.[21,25,27,37,41,44] The size of the clusters varied from 5 nm to 200 nm. They consist of a central region, surrounded by prismatic dislocation loops, ordered along twelve <110> axes. The central region consists of a compact accumulation of dislocations, and contains complexes of two types: triangular, with dimensions 0.5–8 nm, and spherical, with dimensions 5–8 nm.[25,40] The chemical nature of the clusters is not clear, but studies have shown that there is an excess of indium at the points where they are situated. A model has been proposed[37] for the production of the clusters, based on the interaction of antistructural defects with moving dislocations.

Dislocation clusters with a density of 10^2–10^3 cm^{-3} have been detected[27] in non-doped single crystals of indium phosphide and in specimens doped with germanium. No relationship was detected between the germanium concentration and the appearance of the clusters. The distribution of the clusters along the length of the ingot was regular, although some specimens showed a decrease in their density towards the end of the ingot. The density of the clusters increased with increase in the quantity of macroscopic defects (such as twins). After annealing the specimens at 800 °C for 1, 4, and 8 h, the density of the clusters increased from 1.8×10^2 cm^{-2} to 4.3×10^2 cm^{-2}. If the specimen did not contain clusters, they were not formed during annealing. An important characteristic of the annealing was the increase in the size of the clusters as a result of the enlargement of the dislocation loops, and not an increase in the number of dislocations.

In the opinion of the authors cited,[25,27] the main reason for the appearance of clusters is the presence of water in the flux. The reaction of water with indium phosphide gives phosphorus vapour, whose inclusion leads to the production of stresses and to the formation of clusters. Dehydrating the flux by heating made it possible to obtain crystals without dislocation clusters.

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