36. A.Becker, Trans.Electrochem.Soc., 55, 153 (1922).
37. W.H.Brattain and A.Becker, Phys.Rev., 43, 428 (1933).
38. P.Lukirski, A.Sosina, S.Wekschinsky, and T.Zarewa, Z. Physik, 71, 306 (1931).
39. R.C.L.Bosworth, Proc.Roy.Soc., 150A, 58 (1935).
40. I.Langmuir and I.B.Taylor, Phys.Rev., 40, 433 (1932).
41. I.Langmuir and I.B.Taylor, Phys.Rev., 44, 423 (1933).
42. M.Benjamin and R.O.Jenkins, Nature, 143, 279 (1939).
43. E.W.Muller, Z.Physik, 126, 642 (1949).
44. M.Drechsler, Z.Elektrochem., 58, 327 (1954).
45. M.Drechsler, Z.Elektrochem., 58, 334 (1954).
46. M.Drechsler, Z.Elektrochem., 58, 340 (1954).
47. V.M.Gavrilyuk and V.G.Yazeva, Ukrain.Fiz.Zhur., 3, 421 (1958).
48. R.B.Kehoe, R.C.Newman, and D.W.Pashley, Phil.Mag., 1, 783 (1956).
49. K.Schwarz, Z.phys.Chem., 168A, 241 (1934).
50. H.Jedrzejowski, Compt.rend., 194, 1340 (1932).
51. H.Fraunfelder, Helv.Phys.Acta, 23, 347 (1950).
52. Ya.I.Frenkel', "Vvedenie v Teoriyu Metallov" (Introduction to the Theory of Metals), GTTN, Moscow–Leningrad, 1950.
53. A.I.Bykhovskii, Fiz.Metallov i Metalloved., 6, 487 (1958).
54. Ya.E.Geguzin, G.N.Kovalev, and A.M.Ratner, Fiz.Metallov i Metalloved., 12, 42 (1961).
55. G.Tammann, "Metallkunde" (Translated into Russian), ONTI, Moscow, 1935.
56. T.Alty and A.C.Clark, Trans.Faraday Soc., 31, 648 (1935).
57. F.Spiers, Phil.Mag., 15, 1048 (1933).
58. A.I.Bykhovskii, Fiz.Metallov i Metalloved., 6, 487 (1958).
59. A.Bondi, Chem.Rev., 52, 417 (1953).
60. M.A.Bol'shanina and F.P.Rybalko, Zhur.Eksper.Teor. Fiz., 7, 312 (1937).
61. T.Heumann and K.Forch, Z.Metallk., 53, 122 (1962).
62. Yu.V.Goryunov, N.V.Pertsov, B.D.Summ, and E.D.Shchukin, Dokl.Akad.Nauk SSSR, 146, 638 (1962).
63. P.A.Rebinder, M.E.Lipets, M.M.Rimskaya, and A.B.Taubman, "Fiziko-Khimiya Flotatsionnykh Protsessov" (Physical Chemistry of Flotation Processes), Metallurgizdat, Moscow, 1933.
64. B.V.Deryagin, Dokl.Akad.Nauk SSSR, 51, 357 (1946).
65. R.Wenzel, Ind.Eng.Chem., 28, 988 (1936).
66. V.K.Semenchenko, "Poverkhnostnye Yavleniya v Metallakh i Splavakh" (Surface Phenomena in Metals and Alloys), GTTI, Moscow, 1957.
67. V.N.Eremenko, Yu.N.Ivashchenko, V.I.Nizhenko, and V.V.Fesenko, Izv.Akad.Nauk SSSR, Otd.Tekh.Nauk, 7, 144 (1958).
68. V.N.Eremenko and Yu.V.Naidich, Ukrain.Khim.Zhur., 23, 573 (1957).
69. I.L.Rokh, V.V.Ordynskaya, and I.P.Bolotin, Dokl.Akad. Nauk SSSR, 146, 1316 (1962).
70. T.Heumann and K.Forch, Naturwiss., 48, 566 (1961).
71. Yu.V.Goryunov, G.I.Den'shchikova, N.V.Pertsov, B.D.Summ, and E.D.Shchukin, "Tezisy Dokladov na Konferentsii po Poverkhnostnym Yavleniyam v Rasplavakh i v Protsessakh Poroshkovoi Metallurgii" (Abstracts of Papers Presented to the Conference on Surface Phenomena in Melts and in Powder-Metallurgical Processes), Kiev, 1962, p.58.
72. B.D.Summ, Yu.V.Goryunov, N.V.Pertsov, and E.D.Shchukin, Dokl.Akad.Nauk SSSR, 137, 1413 (1961).
73. E.D.Shchukin, Yu.V.Goryunov, G.I.Den'shchikova, N.V.Pertsov, and B.D.Summ, Kolloid.Zhur., 25, 108 (1963).
74. Yu.V.Gorynov, A.P.Dekartov, N.V.Pertsov, B.D.Summ, and E.D.Shchukin, "Tezisy Dokladov na V Vsesoyuznoi Konferentsii po Kolloidnoi Khimii" (Abstracts of Papers Presented to the Fifth All-Union Conference on Colloidal Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1962, p.76.
75. E.D.Shchukin, B.D.Summ, Yu.V.Goryunov, N.V.Pertsov, and A.V.Pertsov, Kolloid.Zhur., 25, 253 (1963).
76. E.D.Shchukin, Candidate's Thesis, Institute of Physical Chemistry of the USSR Academy of Sciences, Moscow, 1957.
77. J.C.Fischer, J.Appl.Phys., 22, 634 (1951).
78. R.T.P.Whipple, Phil.Mag., 45, 1225 (1954).
79. D.McLean, "Grain Boundaries in Metals" (Translated into Russian), Metallurgizdat, Moscow, 1960.
80. M.Hansen and K.Anderko, "Constitution of Binary Alloys", (Translated into Russian), Metallurgizdat, Moscow, 1962.
81. B.D.Summ, Yu.V.Goryunov, N.V.Pertsov, E.D.Shchukin, and P.A.Rebinder, Dokl.Akad.Nauk SSSR, 136, 1392 (1961).
82. B.D.Summ, Yu.V.Goryunov, N.V.Pertsov, V.Yu.Traskin, and E.D.Shchukin, Fiz.Metallov i Metalloved., 14, 757 (1962).
83. V.V.Shuleikin, Dokl.Akad.Nauk SSSR, 147, 92 (1962).

Faculty of Chemistry,
Lomonosov Moscow
State University

U.D.C. 537.311.33

METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

V.N.Vigdorovich and A.Ya.Nashel'skii

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1. INTRODUCTION

Among the semiconducting materials used in present-day electronics and radio technology, a number of chemical compounds covering a wide range of physical properties in different combinations occupy an important place. These are finding increasing application in modern technology, and their number is growing.

In many cases, great difficulty has been encountered in developing methods of preparation of compounds with semiconductor properties. Whereas the well-established techniques of silicon and germanium production could be applied directly to some of these materials, many semiconducting compounds have needed far more complex apparatus and production techniques because of the high reactivity of the compounds themselves (and of their constituent elements), and because of the high melting points and dissociation pressures involved. However, many different preparation techniques, highly relevant to semiconductor technology, have already been established (synthesis, purification, doping, and single-crystal growth).

Apart from a number of unrelated communications, describing individual apparatus and production techniques, the technical literature contains very few critical reviews of our fund of experimental knowledge. Folberth[1] has published a fairly comprehensive survey of the methods of preparation of semiconducting compounds of the $A^{III}B^{V}$ group, including a physicochemical discussion of the nature of these compounds. The methods of preparation of various compounds are dealt with, to some extent, in a number of monographs[2-6] and proceedings of conferences[7-14]. Goryunova[15] and Borshchevskii[16] have reviewed the methods of preparation and the properties of compounds which exhibit semiconductor properties. There are also two bibliographic reviews, edited by Zhuze[17,18].

2. CLASSIFICATION OF THE METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Folberth[1] proposed that the method of preparation of semiconducting compounds should be classified in accordance with the physicochemical properties of the compounds themselves: (1) compounds whose vapour pressure is negligible at the melting point (antimonides); (2) compounds having a significant vapour pressure at their melting point (arsenides and phosphides of indium and gallium); (3) compounds with high melting points and high vapour pressures over the melt (aluminium arsenide and phosphide, nitrides, borides).

Hilsum and Rose-Innes[2] have divided the basic methods of preparation of semiconducting compounds (of the $A^{III}B^{V}$ type only) into four groups: (1) crystallisation from stoichiometric melts (gallium and indium antimonides and arsenides); (2) crystallisation from non-stoichiometric melts (phosphides); (3) condensation from the vapour phase (indium and gallium arsenide and phosphide), including iodide methods; (4) chemical reactions (aluminium, boron, and gallium phosphides and nitrides).

This subdivision of techniques is valuable from the point of view of technology, because the methods of the first two groups enable the compounds to be produced in single-crystal or coarsely crystalline form, whereas the third and fourth groups lead to fine needlelike and platelet crystals, and to films[2]. Hilsum and Rose-Innes' classification[2] is more rational than Folberth's[1].

In the present article, we shall consider the known methods of preparation of semiconducting compounds under two headings: direct and indirect. The criterion for this classification is the chemical nature of the substances used as starting materials, irrespectively of their state of aggregation.

The direct methods are those in which the starting materials are components of the compound being synthesised. Since these methods are closely concerned with crystallisation — the production of compounds in a single-crystal or coarsely polycrystalline form — they had already reached a high stage of development in connection with technologically simpler compounds, and gave satisfactory results with relatively minor modifications.

The direct methods of preparation of semiconducting compounds consist, as a rule, in bringing together the starting components and removing the reaction product from the reaction zone by converting it into a different state of aggregation. The synthesis can be carried out either continuously or batch-wise. The initial mixture of starting components can be gaseous, liquid, or solid, or it can be a mixture of phases in different states of aggregation. The compound must be produced in the solid state, however, and therefore the most important processes are crystallisation from solution, from the melt, and from the vapour phase, since these lead to crystalline products.

It may be impossible to bring the starting components into direct contact: in this case a carrier must be used. The simplest carrier is a neutral gas.

Thus, the direct methods can be subdivided according to the nature of the process leading to the formation of the crystalline compound (crystallisation; condensation with formation of a solid or liquid compound, followed by crystallisation if the compound is obtained in the liquid form; sintering, which is based on the diffusional transport of the components; etc.).

However, if even a single participant of the reaction is a chemical compound able to react with the other components or constituents of the starting mixture, the method of synthesis should be termed "indirect". Methods of this type are often referred to as "chemical methods" in the literature[2]. In most cases the compounds are produced in a crystalline form, but finely divided.

According to the type of reaction employed, indirect methods can be subdivided into two groups: (1) methods relying on double decomposition reactions, and (2) methods relying on thermal decomposition reactions. Reactions of both types may also occur together.

The reactions can take place in a homogeneous or a heterogeneous medium. This has a profound effect on the design of suitable apparatus; the classification of synthetic methods should therefore include this aspect.

Methods of synthesis relying on reactions in a homogeneous phase can be divided into gas-phase (or vapour-phase) methods, and methods of preparing compounds from condensed phases.

In the gas (or vapour) phase, compounds can be synthesised in a stream of carrier gas or in a stream of one of the reactants.

Indirect methods are often used as preliminary synthetic operations, followed by conversion of the resulting compounds into compact specimens, or single crystals, by one of the direct methods. We therefore propose to discuss first the indirect methods, and then the direct methods of preparing compounds.

The indirect methods usually afford crystalline compounds in a highly disperse form. Nevertheless, they have been widely applied in the synthesis of high-melting, decomposable compounds having high dissociation pressures and high chemical reactivity.

The classification of methods for the preparation of semiconducting compounds presented here is, undoubtedly, neither definitive nor complete. Other grounds on which to base a classification could probably be suggested. However, it has enabled us to assign to well-defined classes all published preparative methods of which we were aware, and to arrange the present review within the framework of an explicitly stated classification.

3. INDIRECT METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Reactions in the Condensed Phase

Reactions in the condensed phase are used comparatively seldom.

Montignie[19] prepared aluminium phosphide by heating a mixture of red phosphorus, aluminium oxide, and potassium cyanide in a closed crucible. The product, which was a mixture of aluminium phosphide and phosphate, was treated with hydrochloric acid, which dissolved the phosphate (and some of the phosphide). The insoluble residue, heated to 600°, was found to be aluminium phosphide of stoichiometric composition.

Effer and Antell[20,21] prepared the phosphides and arsenides of indium and gallium by oxidation–reduction reactions between a chloride of the metal and the metalloid:

$$3GaCl_2 + As \rightarrow 2GaCl_3 + GaAs$$

or

$$2InCl + P \rightarrow InCl_2 + InP,$$

or between a chloride of the metalloid and the metal:

$$AsCl_3 + 2In \rightarrow InCl_3 + InAs.$$

To prepare gallium arsenide, liquid gallium dichloride was heated at 500° for 24 h with powdered arsenic in a nitrogen atmosphere. The resulting gallium arsenide was mechanically separated from the small amount of gallium formed by the reaction, and heated *in vacuo* at 600°.

Metal phosphides have been prepared by the reaction between liquid white phosphorus and indium monochloride (or gallium dichloride) at 300° in a nitrogen atmosphere for 1 h. The complex compounds produced by the reaction were decomposed by heating the mixture to 500°, giving indium or gallium phosphide.

Arsenic trichloride and indium, in stoichiometric proportions, were heated to 350° in evacuated and sealed bulbs. The free end of the bulb was then moved out of the furnace, and the end containing the reaction product was heated to 600°. This caused the volatile materials which had escaped reaction to condense on the cold end of the bulb. The yield of arsenides was in excess of 95%; that of phosphides ~ 65%.

Addamiano[22] used a different type of reaction in the condensed phase to prepare phosphides:

$$2M + Zn_3P_2 \rightarrow 2MP + 3Zn,$$

where M = Al, Ga, or In. The reaction was carried out in a stream of argon in order to carry away the zinc vapour and to protect the reactants from oxidation. Aluminium phosphide was synthesised at 1000–1100° in the course of 30 min, gallium phosphide at 800° in 12–24 h, and indium phosphide at 700–800° in 24–48 h. The yield of final product was very small in the last reaction.

Reactions in the Vapour Phase

Reactions in the vapour phase have been widely used in the preparation of a great variety of semiconducting compounds.

Frerichs[23] grew crystals of cadmium sulphide by the reaction between cadmium vapour and hydrogen sulphide in a stream of hydrogen. The cadmium was placed in a boat heated to 800–1000°. The hydrogen sulphide was introduced into the reaction close to the boat, where it became mixed with the cadmium vapour. The cadmium sulphide produced was deposited on the walls of the reactor as crystalline platelets 20 × 30 × 0.22 mm in dimensions. Cadmium selenide and telluride crystals can also be grown by this method.

Gershenzon and Mikulyak[24] synthesised gallium phosphide crystals by a different method, based on the reaction between vapours of phosphorus and gallium monoxide in a closed volume. Gallium monoxide vapour was generated by the reaction

$$Ga_2O_3 + 4Ga \rightarrow 3Ga_2O.$$

A quartz dish containing a mixture of gallium trioxide and gallium in 1 : 4 molecular proportions was placed at the upper end of an evacuated and sealed quartz bulb. The lower end of the bulb contained red phosphorus. The bulb was inserted vertically into a furnace designed to keep the upper end of the bulb at 975–1060°, and the lower end at 350–400°. The two regions of controlled temperature were joined by a smooth temperature gradient. The gallium monoxide vapour migrates towards the cooler end of the bulb, where it reacts with the phosphorus vapour:

$$5Ga_2O + 3P_4 \rightarrow 10GaP + P_2O_5.$$

This reaction produces needlelike crystals of gallium phosphide, 1–20 mm long, on the walls of the bulb. In some cases the reaction is carried out in a stream of inert gas. Effer and Antell[21] prepared gallium arsenide by passing gallium dichloride and arsenic vapour, in a stream of pure nitrogen, through a heated quartz tube. The vapours were led to a mixer from separately heated generating flasks. The gas mixture in a stream of carrier gas was introduced into a quartz tube at 800°, and thence into another tube at 600° where gallium arsenide crystals were deposited as a fine powder and separated from the unreacted volatile materials. A yield of final product as high as 75% was obtained in one experiment.

Reactions in Heterogeneous Media

Reactions in heterogeneous media, like those in the vapour phase, have been widely used to synthesise various types of semiconducting compound.

A good example is the method of preparation of gallium phosphide developed by Samsonov *et al.*[25], who reduced gallium trioxide with phosphine:

$$Ga_2O_3 + 2PH_3 \rightarrow 2GaP + 3H_2O.$$

The reaction was carried out in a tube furnace at 950° for several hours. The phosphine was generated by decomposing aluminium phosphide with water. A similar process was proposed by Lewis[26], who reduced gallium trioxide with phosphorus vapour at 1000° in a stream of argon or argon–hydrogen mixture. The resulting gallium phosphide powder (particle size 1 μm) was densified by recrystallisation at 1050° for several hours.

Semiconducting compounds can be used as starting materials. Thus, Addamiano[27] synthesised aluminium nitride by nitriding aluminium phosphide with ammonia:

$$AlP + NH_3 \rightarrow AlN + \tfrac{1}{4}P_4 + \tfrac{3}{2}H_2.$$

Powdered aluminium phosphide was heated at 1000–1100° in a stream of ammonia for 1–2 h. Gallium nitride was prepared by the same method and under the same conditions by using gallium phosphide or arsenide in place of aluminium phosphide.

Although organometallic compounds should, in principle, lead to purer synthetic materials, their use in the preparation of semiconducting compounds has been rather limited. A patent application by Didchenko[28], claiming the preparation of indium phosphide by the reaction between an organometallic compound of indium and phosphorus in a hydrogen stream at 300°, is one of the few publications dealing with this problem. By working at lower temperatures, it should of course be possible to minimise by this method the contamination of the final product arising from interactions with the apparatus and with the atmosphere.

Another example of the use of heterogeneous reactions in the synthesis of semiconducting compounds is Tsymbalov and Trushina's low-temperature synthesis[29] of gallium selenide by passing gaseous hydrogen selenide through a solution of gallium trichloride at pH 6.5–7 and at a temperature of ~ 80°.

Mill' and Naumova[30] prepared ferrite crystals ($Y_3Fe_5O_{12}$) with a garnet structure from aqueous solutions containing Y_2O and Fe_2O_3 in proportions between 3 : 1 and 1 : 10. The reaction was carried out under autoclave conditions (1500 atm, 500°) during 5–15 days. The resulting equiaxial crystals had dimension of ~ 1.5 mm.

Thermal Decomposition Reactions

Methods of preparation of semiconducting compounds based on the thermal decomposition of more complex starting materials are relatively seldom used. A typical example is Renner's procedure[31] for the preparation of aluminium, gallium, and indium nitrides by decomposition of their monoammines in the vapour form ($MCl_3.NH_3$, where M = Al, In, or Ga) on a hot substrate. A graphite disc, which can be heated by a high-frequency induction heater, is placed in a quartz bulb within a quartz tube. The monoammine of the desired metal is heated in a separate electrical resistance furnace. The preparation conditions requiring control include the temperatures of the substrate and of the monoammine, and the pressure in the bulb. The perfection of the crystals deposited on the substrate can be improved by rotating the graphite disc. Substrate temperatures were controlled (with rotation of the crystals) at 1000–1400° for AlN, ~ 1000° for GaN, and 600° for InN.

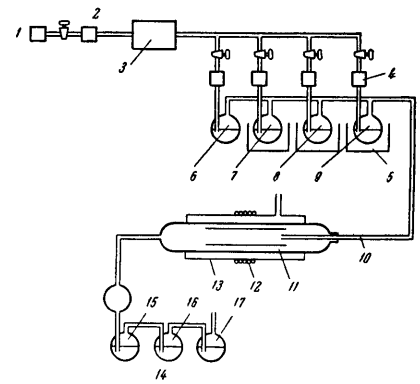


Fig.1. Apparatus for preparing silicon carbide single crystals by thermal decomposition of a gas mixture:
1) hydrogen supply; 2) pressure reducing valve;
3) gas purifier; 4) flow meter; 5) thermostats;
6) mineral oil; 7) silicon tetrachloride; 8) toluene;
9) compound of the doping element;
10) inlet for gas mixture; 11) graphite tube;
12) high-frequency induction coil;
13) water-cooled jacket; 14) scrubbers for side-products;
15) mineral oil; 16) methanol; 17) alkali solution.

To prepare crystalline silicon carbide, Ellis[32] decomposed a mixture of gases which he introduced, in a hydrogen stream, into a quartz reactor containing a graphite cylinder heated by an external high-frequency set (Fig. 1). The silicon-containing gas was silicon tetrachloride or trichlorosilane vapour; the carbonaceous gas was toluene, methane, carbon tetrachloride, or chloroform. The single crystals obtained had a diameter of 4–5 mm.

4. DIRECT METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Condensation

Condensation is used in the direct synthesis of compounds from their components.

Bishop and Liebson[33] prepared crystals of cadmium sulphide by the following method. Metallic cadmium was heated to 650°, and sulphur to a temperature above 400°. The reaction chamber had a temperature of 1000°. The vapours of the components were transported to the reaction chamber by separate gas streams of argon–hydrogen mixture. CdS crystals condensed on the walls of the reactor as platelets a few square centimetres in area and up to 1 mm thick.

Scharowsky[34] prepared zinc oxide crystals in an apparatus in which the zinc was heated to 600° in a stream of nitrogen containing 1% of hydrogen. This carried the

zinc vapour to a reactor at 1150° connected to atmosphere. ZnO crystals grew on the walls in the form of needles up to several centimetres in length and 0.2 mm thick.

Sintering

Semiconducting compounds have been prepared by sintering [35,36].

Goryunova and coworkers [35] obtained small crystals of indium phosphide of stoichiometric composition by heating a compact of indium and phosphorus powders. The excess of phosphorus was distilled off by heating *in vacuo*. Watson [36] prepared cadmium and zinc sulphides, selenides, and tellurides by gradually heating the powdered elements to 450° at a rate of 0.5 deg min^{-1} in a vacuum.

Resublimation

Sublimation has been frequently used in the preparation of infusible semiconducting compounds [37-39].

Reynolds and Czyzak [37] grew single crystals of zinc sulphide from powdered zinc sulphide in a sealed quartz bulb filled with hydrogen sulphide at 0.42 atm pressure. The bulb was heated to 1250° for 2–4 days, with a smooth temperature gradient along its length. The single crystals obtained by this method had dimensions of 2 × 2 × 10 mm. Crystals of cadmium sulphide were prepared by a similar technique [38].

Cadmium sulphide has been resublimed in a stream of inert gas (helium) [39]. The compound was doped, during the sublimation, with a component placed in a separately heated zone. A temperature gradient of 10–40 deg mm^{-1} was established along the length of the furnace. The crystals were obtained as a condensate on a water-cooled tube, and had needlelike and platelet habits.

The resublimation method is the main method of preparation of silicon carbide crystals at present [40-44]. Lely [40] was among the first to use it. The raw, granular silicon carbide was loaded into a container between two coaxial graphite cylinders. The inner cylinder had a number of orifices through which the silicon carbide vapour could penetrate to the cooler central region. The cylinder was heated in a furnace to 2500–2600° for 6–8 h. The process was carried out in a hydrogen, argon, or carbon monoxide atmosphere. A radial temperature gradient, from the outer to the inner cylinder, was maintained in the furnace: crystal growth occurred along this gradient. The crystals obtained were ~ 10 mm long and 2–3 mm thick. The silicon carbide crystals were doped by introducing volatile phosphorus, aluminium, or boron compounds into the furnace atmosphere.

The method was later used with minor modifications [41,42], such as operation in a vacuum or under pressure, the use of seeds, and of different kinds of container, etc.

Some very recently developed resublimation methods form a special group of procedures for the preparation of compounds by condensation from the vapour phase.

These processes occur *via* the dissociation of the compound. The components interact with the vapour of a "third" component, forming volatile compounds, in the hotter regions. The volatile compounds diffuse to the cooler regions, where they dissociate to give products capable of interacting to re-form the desired compound. Reactions of this type have been termed "transport" reactions [43].

Transport reactions are most commonly used for growing epitaxial layers of semiconducting compounds on oriented single-crystal substrates of germanium, silicon, or other semiconductors. The deposits can be doped to the desired conductivity type and physical properties by introducing into the reaction tube small amounts of zinc, cadmium, magnesium, aluminium, or other metal chlorides. Different types of $p-n$ junctions can be produced [44] by depositing a compound of one conductivity type on a substrate of the opposite conductivity type.

Antell [45] prepared large crystals of gallium phosphide by resublimation in the presence of iodine vapour in the apparatus shown schematically in Fig. 2. Resublimation proceeds by the reactions

$$3GaP + 3I \rightarrow 3GaI + 3P,$$
$$3GaI + 2P \rightarrow GaI_3 + 2GaP.$$

The starting crystals were maintained at a temperature of ~ 1000°. New crystals grew on the walls where the temperature was ~ 800°. The concentration of iodine vapour in the bulb was ~ 1.2 mg cm^{-3}. Gallium phosphide crystals were prepared [46] by a similar method, using hydrogen as the transporting agent. Ikada and Kano [47] prepared gallium arsenide by this method, using single-crystal germanium as a seed. In contrast to previous workers, Newman and Goldsmith [48] prepared gallium arsenide crystals in a stream of hydrogen and hydrogen chloride rather than in sealed ampoules.

Crystallisation

The most widely used methods of preparation of compounds rely on the process of crystallisation. This large group of methods can be further subdivided according to the mode of crystallisation involved: normal freezing; normal directional freezing (the Bridgman–Stockbarger method); pulling from the melt (the Czochralski–Kyropoulos method); zone melting (Pfann's method); the Verneuil method; etc. The methods of fractional crystallisation shown diagrammatically in Fig. 3 are very useful technologically for compounds which decompose. The Verneuil method is similar in principle to zone recrystallisation, but it has not been used in its original form for the preparation of semiconducting compounds.

Fractional crystallisation from the melt to give a compounds shows some features which depend on whether the

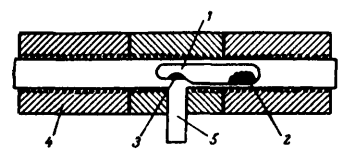


Fig. 2. Apparatus for preparing single crystals of gallium phosphide or gallium arsenide by resublimation in iodine vapour:
1) quartz ampoule filled with iodine vapour; 2) crystalline charge of the desired compound; 3) growing crystal; 4) three-zone furnace; 5) side-tube with inspection window.

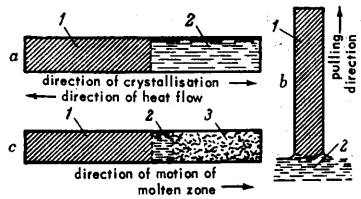


Fig.3. Basic fractional crystallisation methods:
a) normal directional freezing;
b) pulling from the melt (produces specimens of variable composition);
c) zone recrystallisation;
1) crystallised section; 2) melt; 3) solid charge.

process is carried out horizontally or vertically. The vertical variants of the zone recrystallisation technique can be operated without a container†.

In the vertical variants, account must be taken of gravity effects on the upward and downward diffusion of the components. Little use has been made as yet of intermediate (inclined) variants.

These methods of crystallisation were originally developed for compounds which do not decompose [49-83].

The work of Usachev *et al.* [49] on the synthesis of mercury selenide and telluride in thick-walled quartz bulbs is an example of the preparation of compounds by normal (free) crystallisation. A mixture of mercury and powdered selenium or tellurium was heated to 800° or 675° respectively over a period of 6–8 h, kept at this temperature for 20–30 min, and slowly allowed to cool. Kolomoets and Popova [50] prepared aluminium antimonide by melting the components in an alundum crucible within an evacuated quartz bulb. After the synthesis had taken place at 1200°, the bulb was inverted and the melt was cast into a hollow stopper made of graphite. Normal crystallisation was then allowed to proceed in this graphite crucible.

Often, compounds are prepared by direct fusion of the components, with normal crystallisation from the melt, followed by subsequent directional crystallisation.

The method of normal directional freezing for the preparation of compounds is known as the Bridgman–Stockbarger method, and can be carried out in both the horizontal and the vertical variants. The apparatus needed for the Bridgman–Stockbarger process is basically of simple design. Difficulties arise in the choice of suitable container materials, or in the special treatment of the surface of the container which is in contact with the melt.

The normal directional freezing method (after Bridgman) is commonly used for the synthesis, purification, and doping of compounds which do not decompose, in both the horizontal and the vertical variants [51-54].

Hazelby and Parmee [51] prepared aluminium antimonide by pulling a boat containing the melt through the furnace at 2 mm min^{-1} (horizontal variant). Vertical variants of the normal directional freezing method were used by Lawson [52] and by Harman [53].

Lawson [52] grew single crystals of lead sulphide, selenium, and telluride at rates of 0.017–0.17 mm min^{-1}. Since a sealed container (bulb) is used, the method is not suitable for compounds which expand on solidification, such as indium antimonide, gallium antimonide, and others. Mercury selenide was obtained as a coarsely crystalline ingot by a vertical variant of Bridgman's method [53] at a growth rate of ~0.05 mm min^{-1}.

Crystals of mercury and cadmium telluride were grown [54] at 0.04 mm min^{-1} in a furnace with a temperature gradient, with the charge arranged vertically.

Crystal pulling from melts by the methods of Czochralski and Kyropoulos‡ is also widely used in the preparation, purification, and doping of compounds which do not decompose. The pulling is carried out in the vertical direction, and upwards. Horizontal variants of this method, or vertical variants with downward pull, have not so far been reported.

Large single crystals of indium antimonide have been pulled from the melt by the Czochralski–Kyropoulos method [2,56,57]. A quartz crucible was used.

Mirgalovskaya and Matkova [58] prepared single crystals of indium antimonide by Czochralski's method using a quartz crucible. The pulling rate was 0.7–0.8 mm min^{-1}, and the crucible and the seed were rotated at 4–5 revolutions per minute and 3–4 revolutions per minutes respectively.

Single crystals of aluminium antimonide were prepared by pulling from the melt in an apparatus originally designed for the growth of germanium and silicon single crystals. Using graphite or sintered alumina crucibles [59-61], Mirgalovskaya and Strel'nikova [62] prepared single crystals of aluminium antimonide by Czochralski's method. With alumina crucibles and a helium atmosphere, the pulling rate was 0.7 mm min^{-1}, and the seed and the crucible were rotated at 2 revolutions per minute in opposite directions.

Zone melting is a very popular method of synthesising, purifying, and doping semiconducting compounds [5,6,63].

Indium antimonide was zone-melted in quartz boats in order to purify and to homogenise it, using an argon atmosphere [64], vacuum [65], and vacuum with electromagnetic stirring of the molten zone [66]. Mirgalovskaya and Matkova [58] zone-melted indium antimonide at a crystallisation velocity of 0.2 mm min^{-1}, and obtained large-grained specimens containing 10^{16} cm^{-3} impurity atoms, and having an electron mobility of 82 500 cm^2 V^{-1} s^{-1} at 300°K. Vinogradova *et al.* [67] investigated the purification of indium antimonide by zone melting. Their ingots were 150–350 mm long and 4–7 mm in diameter. The length of the molten zone was 5–50 mm, the rate of crystallisation 0.1–1 mm min^{-1}, and the number of zone passes as high as 45. The result was

† This technique is called "floating-zone" melting in the English and American literature (Ed. of Translation).

‡ Kuznetsov points out [55] that crystal growth from the melt can be carried out by Czochralski's method (the growing crystal is pulled upwards, and simultaneously rotated about its longitudinal axis) and by Kyropoulos' method (the seed remains stationary, and crystal growth proceeds only as a result of the loss of heat from the charge). Some non-Soviet authors [1,6,56,57] fail to make a clear distinction between these principles of crystal growth.

indium antimonide of the highest reported purity: $2.5 \times \times 10^{13}$ cm^{-3} impurity atoms, and an electron mobility of 400 000 cm^2 V^{-1} s^{-1} at 77°K and 100 000 cm^2 V^{-1} s^{-1} at 300°K.

Gallium antimonide crystals have been prepared[68-70] by direct fusion followed by zone melting. The preparation of aluminium antimonide single crystals by zone melting has also been reported[60,71-73].

All the examples so far discussed refer to zone melting in its horizontal variant, with a container. Crucible-free vertical variants do not appear to have been used, probably because of the high density of semiconducting compounds, coupled with a low surface tension in the molten state, which limits the ingot diameter to 4–6 mm. An analogous situation exists with germanium. Vertical zone-melting methods with a container have not been applied, either because the compounds were too reactive or because of large volume changes on solidification.

In one case, bismuth telluride crystals have been prepared by zone melting in a vertical, sealed quartz tube[74], with a zone 1–2 cm long travelling at 1.0–1.4 mm min^{-1}.

Methods of preparation of congruently melting compounds by crystallisation from non-stoichiometric melts are of interest. Fisner *et al.*[75] obtained single crystals of zinc antimonide by the horizontal form of Bridgman's method in a graphite boat which could be moved along a tube of Vycor glass. The temperature gradient at the solidifying interface was ~ 4 deg mm^{-1}, and the velocity of crystallisation (caused by the motion of the temperature field) was ~ 0.06 mm min^{-1}. Zone melting was used in the same investigation[75] to grow single crystals on a seed, with a 25 mm zone length, a zone temperature of 560–575°, and a crystallisation velocity of ~ 0.18 mm min^{-1}. In both cases crystallisation was carried out from melts of composition 40 at.% Zn + 60 at.% Sb.

Compounds which melt at low temperatures without decomposition are seldom prepared by crystallisation from a non-stoichiometric melt. This method has been used mostly for the preparation of infusible compounds such as silicon carbide (β-modification)[76-81].

A solution of carbon in silicon, prepared by melting the latter in a graphite crucible, is used. We may consider, as an example, the work of Smith[76]. A graphite crucible with lid, containing the molten silicon, was heated to 1600–2200°, with a temperature gradient of 15–36° along the length of the crucible. The process was carried out either in a stream, or under pressure (up to 55 atm) of an inert gas. The melt was then cooled at 1.5–30 deg h^{-1}. The crystals were deposited at the bottom of the crucible, where the temperature was lowest.

Another technique for growing crystals of high-melting compounds relies on crystallisation from solution in a "third" component. Solutions of silicon carbide in iron, nickel, and other metals have been used for this purpose[77,78]. Halden[80] grew silicon carbide crystals by the Czochralski method from a solution of carbon in a melt of 65% Fe + + 35% Si. Large aggregates of crystals were obtained with the melt at 1675–1750°, the seed at 1665°, and a crystallisation rate of 0.06–0.36 mm min^{-1}. Better results were achieved by rotating the graphite crucible. Ellis[81] grew silicon carbide crystals from solutions of SiC in iron, nickel, or silicon, by cooling a quartz crucible containing the melt at 100 deg h^{-1}. The crystals, which had dimensions of the order of 2.5 mm, were isolated by dissolving the matrix in nitric or hydrofluoric acid.

5. METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS PRONE TO DECOMPOSITION

Methods without Pressure Control

When a need for new materials (arsenides, phosphides, etc.) with high melting points and dissociation pressures arose in semiconductor physics and semiconductor device technology, the methods of synthesis, purification, doping, and crystal growing described in the preceding sections did not lead to the desired results. It was found possible to grow small crystals in the laboratory, and to study their physical and electrical properties, but the synthetic methods did not lend themselves to application on an industrial scale.

Initially, experiments on the synthesis of compounds which decompose on heating used the same conditions as those used earlier for stable compounds. A sealed tube containing the components of the desired compound was placed in a single-zone (one-temperature) furnace. These methods, like the other methods of preparation of semiconducting compounds without control of the pressure above the melt, require extremely slow heating rates.

The synthesis of a semiconducting compound (indium phosphide) which decomposes on melting, by direct fusion of the initial components, was first attempted[82] in 1941. However, in spite of very long reaction times, a homogeneous compound could not be prepared by melting together indium and phosphorus in sealed bulbs.

With compounds of appreciably lower vapour pressure (arsenides), very prolonged experiments of this type eventually proved successful.

Landelli[82] prepared specimens of indium arsenide by heating stoichiometric mixtures of indium and arsenic for a long time in sealed quartz tubes. Evans and Jaffe[83] obtained gallium arsenide by the same method.

When these tubes are heated, a solid crust of the compound, crystallised from the melt at a temperature below its melting point, is formed on the surface of the liquid charge. This inhibits the diffusion of the vapours of the volatile constituents of the melt, and lengthens the time required for the synthesis. In order to speed up the synthesis, shaking[84,85], vibration[16,86], and rotation[87] of the tube have been tried, in the hope of fracturing the crust of compound and thus facilitating diffusion.

Borshchevskii[16,86] created more favourable conditions for the synthesis of various $A^{III}B^{V}$ compounds liable to decomposition, and of solid solutions of such compounds, by applying low-frequency vibrations from a magnetostrictive device.

Shafer and Weiser[87] prepared indium phosphide by the direct fusion of a mixture of indium and finely divided phosphorus in a sealed quartz tube, which was rotated at 60 revolutions per minute in a horizontal furnace. The purpose of rotating the tube was to prevent the formation of a crust on the surface of the reaction mixture. When the temperature was slowly raised to 820° over a period of 48 h, a porous microcrystalline mass of indium phosphide was obtained. Methods of preparation of decomposable compounds in which pressure control is not provided (single-zone, or single-temperature methods) often produce a mixture of the desired compound with an excess of one of the components, or with the corresponding eutectic. Special methods may be needed to separate the stoichiometric compound from such a mixture, *e.g.* the method of

Wolff *et al.*[88], who prepared single crystals of indium phosphide by normal directional crystallisation of indium-rich indium–phosphorus melts. Crystals of indium phosphide up to 12 mm long and 1.5 mm thick were isolated after removing the excess of indium with a solution of hydrochloric acid in glycerol at 180°. Not surprisingly, the yield of indium phosphide under these conditions was not high.

Recently, a method of preparation of compounds liable to decomposition has come to the fore, in which the pressure is essentially uncontrolled. The volatility of the compound itself and of its components is significantly depressed by the kinetic effect of a high pressure of inert gas introduced above the melt. In practice, an inert gas pressure about 100 times higher than the equilibrium dissociation pressure is adequate. The method is particularly successful in the preparation of compounds undergoing dissociation to give a high vapour pressure of both components (group $A^{II}B^{VI}$ compounds).

Shternberg *et al.*[89] used this method to prepare lead and zinc sulphide single crystals under 100–200 atm of nitrogen by normal directional freezing, the melt being cooled at 1 deg min^{-1}. The controlled, technological preparation of compounds liable to decomposition became possible as a result of the work of Gans *et al.*[90], who achieved control over the pressure in a tube containing the components of the desired compound by separately controlling the temperature of a condensate of the more volatile constituent (two-region, or two-temperature method).

This method formed the basis of later apparatus and technological procedures for the production of semiconducting compounds with high dissociation pressures.

The theoretical concepts underlying the preparation of semiconducting compounds showing dissociation, including phase equilibrium studies, the influence of external pressure on the nature of the interaction between components, the types and the actual forms of the phase diagrams for incongruently subliming compounds, have been discussed by a number of authors[1,87,91-93]. The work devoted to these problems has greatly assisted the search for new methods of preparation of compounds liable to decomposition.

Methods with Control of the Vapour Pressure of the More Volatile Component

Crystallisation methods of preparation of compounds prone to decomposition involving control of the vapour pressure of the more volatile component above the melt can be divided into three groups.

If the vapour pressure of the volatile component within the tube is controlled at the level which enables its solution in the melt to retain a stoichiometric composition, the crystallisation proceeds congruently, *i.e.* the compound is deposited as crystals of stoichiometric composition from a stoichiometric melt.

The vertical variant of the normal directional crystallisation method has not been used any more with these compounds than with compounds which do not decompose, because of the large volume changes on solidification, which tend to break the container.

The horizontal variants have been used by several workers. Harman *et al.*[94] prepared indium arsenide in the apparatus shown diagrammatically in Fig. 4. An evacuated

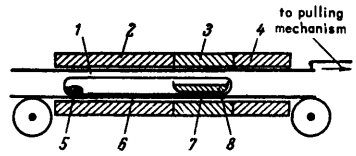


Fig.4. Apparatus for preparing indium arsenide crystals by directional crystallisation (horizontal variant):
1) evacuated and sealed quartz ampoule;
2) furnace set for 560°;
3) furnace set for 1000°;
4) furnace set for 900°;
5) condensate of the more volatile component (arsenic);
6) refractory tube (mullite);
7) quartz boat;
8) indium arsenide melt.

quartz bulb, containing the melt, was drawn through a series of heaters kept at 560°, 1000°, and 900°. The first of these controlled the arsenic vapour pressure in the tube at the desired value (0.33 atm). The second kept the charge in the molten state. The third was intended to relieve the stresses in the crystal. The pulling rate was 0.3–0.8 mm min^{-1}.

Harada and Straust[95] used essentially the same method to prepare indium arsenide single crystals, but they coated their quartz boat with graphite, and conducted the crystallisation at ~ 0.05 mm min^{-1} in a temperature gradient of 18 deg cm^{-1} at the solidification front.

Cunnell *et al.*[96] and Weisberg *et al.*[97] applied this method to the preparation of gallium arsenide.

Compounds have also been prepared by pulling from a melt of stoichiometric composition in a two-zone (two--temperature) furnace. These are best discussed from the standpoint of the constructional features of the particular apparatus employed.

The first such apparatus was described by Gremmelmaier[98], who pulled his crystals in a vertical, evacuated quartz tube located in a two-zone furnace. The seed was raised, and rotated, by means of external magnets which reacted on an iron core within the tube. An apparatus of this type, used in a later investigation[97] for the preparation of gallium arsenide single crystals, is shown in Fig. 5.

Richards[99] described a different design of an apparatus for seed-pulling from the melt of semiconducting compounds liable to decompose. Instead of a sealed tube, he used a hydraulic seal of liquid metal (gallium or indium). The internal pressure was balanced by a controlled external gas pressure. The apparatus was intended for the preparation of indium and gallium arsenide crystals. This construction does not appear to have been widely used.

The next development was a design by Moody and Kolm[100], who relied on the "syringe" seal (Fig. 6) which subsequently became very popular in floating-zone melting as well as in crystal pulling apparatus[97,101,102]. The principles of zone--melting decomposable semiconducting compounds were first established by Boomgard *et al.*[103] The walls of the tube, containing the components of the desired compound or the compound itself, are heated to the temperature at which the vapour pressure of the more volatile constituent is the

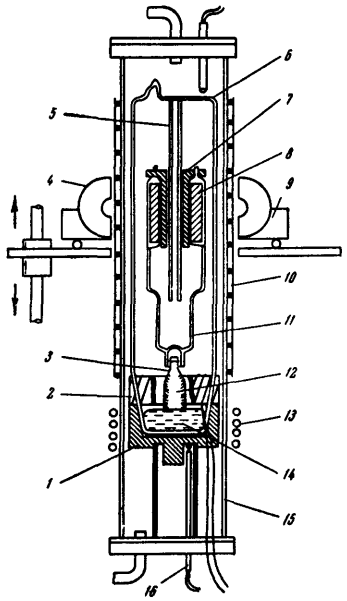


Fig.5. Magnetic-drive apparatus for preparing single crystals of gallium arsenide by pulling from the melt:
1) graphite crucible;
2) transparent heated screen;
3) seed;
4) permanent magnet;
5) quartz guide tube;
6) evacuated and sealed quartz tube;
7) graphite bush;
8) soft-iron cores;
9) magnet rotating mechanism;
10) external heater for tube walls;
11) quartz coupling with seed holder;
12) growing crystal;
13) high-frequency induction coil;
14) melt; 15) external quartz tube filled with inert gas; 16) thermocouple.

same as its vapour pressure over the melt. The liquid zone is kept at a temperature slightly above the melting point of the compound.

Since it is difficult, in practice, to keep the temperature at a constant level over the whole length of the tube (in single-crystal growing, for example), the condensate of the volatile component (see Fig. 4) is transferred to a separate, independently heated part of the tube. The temperature of this part of the tube must be controlled with high precision.

The horizontal variant of zone melting has been used to prepare compounds which tend to decompose [96,104,105].

Cunnell *et al.*[96] purified gallium arsenide by this technique, using high-frequency currents to heat the molten zone. Effer[104] purified gallium arsenide by induction heating, at a rate of crystallisation of 0.6–0.7 mm min^{-1}.

Richards[105] described an interesting horizontal zone-melting procedure, combining purification of gallium arsenide with single-crystal growth. A tube containing the charge was placed inside an alundum tube, heated by an internal winding. A thermally insulating block of firebrick, externally located, could be moved along the tube. The temperature inside this block reached ~1240° when the

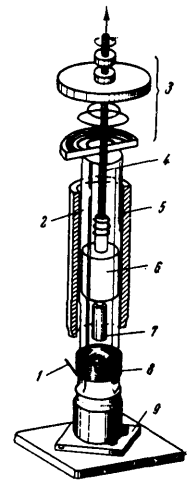


Fig.6. "Syringe" seal apparatus for preparing gallium arsenide single crystals by pulling from the melt:
1) high-frequency induction coil;
2) quartz chamber;
3) coupling seal; 4) coupling;
5) heater for tube walls;
6) quartz piston, internally ground to the chamber wall;
7) seed; 8) crucible with melt;
9) supporting platform.

tube was heated to 800°. The vapour pressure of arsenic inside the sealed tube was controlled by a separate heater.

Vertical zone melting of semiconducting compounds which decompose is carried out without a crucible. Two types of apparatus can be used.

Whelan and Wheatley[106] arranged the ingot within the tube so that the upper part was supported and the lower part was clamped. After the molten zone had been established, the distance between the upper and the lower part of the ingot was kept constant. A similar method was used by Cunnell *et al.*[96], Weisberg *et al.*[97], and Cunnell and Wickam[107] (for gallium arsenide), and by Frosch and Derick[108] for gallium phosphide.

Cunnell and Wickham[107] include the "syringe" seal principle in their apparatus, which enabled them to control the outline of the molten zone. The material zone-refined was gallium arsenide.

Use of Balancing Pressure

The methods and apparatus so far described have been used mainly for arsenides, whose dissociation pressures can be withstood by quartz tubing. However, the strength of quartz tubing proved insufficient for zone-melting phosphides, and balancing pressures had to be applied.

Balancing pressure is used for two purposes: to support the walls of the ampoule[108] and to hinder the diffusion of the volatile component through a seal[109].

Frosch and Derick[108] zone-melted gallium phosphide in a thick-walled steel autoclave inside which were two furnaces

for heating a sealed quartz tube. The latter contained a quartz or graphite boat, centrally located by two lengths of quartz tubing, and could be moved by means of a rod passing through a sliding seal. The molten zone was generated by a high-frequency induction heater.

Fischer[109] described the melting and normal crystallisation of gallium and boron phosphides in autoclaves. The high external pressure suppressed the diffusion of the volatile component out of the ampoule through a narrow (capillary) vent.

Crystallisation from Non-Stoichiometric Melts

Compounds can be prepared from non-stoichiometric melts replenished either through the vapour phase or by a condensed phase. There are many examples[110-115] of the preparation of crystalline compounds by the horizontal, normal directional freezing method.

Crystallisation from a non-stoichiometric melt depletes the melt of one of its components. This can be easily fed back into the melt by dissolution from the vapour phase by means of a condensate of this component in the free volume of the reaction bulb[1,91].

Harman and coworkers[110] prepared indium phosphide by crystallisation of non-stoichiometric melts of indium and phosphorus (35 at.% P) in a three-zone furnace similar to the one shown in Fig. 4. However, crystallisation was induced not by moving the boat through the composite furnace used to generate the required temperature gradients, but by causing the whole temperature profile to move relatively to the fixed ingot. This was achieved by decreasing the power supplied to the heaters.

Harman's apparatus[110] has been used, with only slight modifications, by Weisberg *et al.*[97], Nashel'skii and Ostrovskaya[111], and Guire and Weiser[112], who grew crystals of indium phosphide, and by Strambaugh and coworkers[113], who grew gallium phosphide.

A vertical variant of the normal directional crystallisation method is described in a paper by Vieland and Skalski[114], who prepared gallium arsenide crystals from gallium-rich (Fig. 7) or arsenic-rich melts. Melts of the first type, containing 10 at.% of arsenic, were heated to 900° and crystallised at ~ 0.007 mm min^{-1}.

Crystals of indium phosphide were obtained by Harman and coworkers[110] by pulling from a non-stoichiometric melt. The apparatus, which had a magnetic drive, was similar to the arrangement used[98] by Gremmelmaier (Fig. 5). The melt had the composition 35 at.% P. Crystallisation was allowed to proceed at ~ 0.08 mm min^{-1}, with with rotation of the seed at 6 revolutions per minute.

The crystallisation of decomposable semiconducting compounds by zone melting of non-stoichiometric melts has only been attempted in the horizontal variant[111,115-118].

Nashel'skii and Ostrovskaya[111] prepared large-grained ingots of indium phosphide in graphite-coated quartz boats 100–150 mm long, using a 20 mm zone and a rate of crystallisation of 0.5 mm min^{-1}. The melt in the zone contained ~ 40 at.% P, and was kept at 1020° by an electrical resistance heater.

Davis[115] produced gallium phosphide crystals in graphite boats under a phosphorus pressure of 3–20 atm. The molten zone was generated by a high-frequency induction heater, and was advanced at the rate of 0.001–0.01 mm × × min^{-1}.

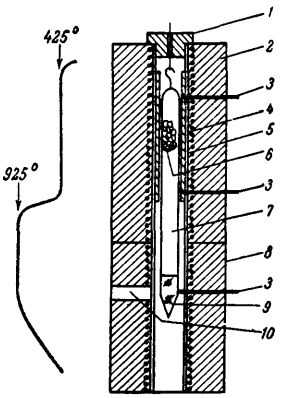


Fig. 7. Apparatus for preparing gallium arsenide crystals by normal directional crystallisation (vertical variant) from non-stoichiometric melts. The temperature profile along the furnace is shown on the left:
1) stopper; 2) low-temperature furnace; 3) thermocouple; 4) steel tube; 5) heater; 6) arsenic; 7) evacuated and sealed quartz ampoule; 8) high-temperature furnace; 9) gallium; 10) inspection window.

Folberth[116] and Nashel'skii *et al.*[117] used zone crystallisation from non-stoichiometric melts in their physicochemical researches. Using this method, Folberth[116] measured the dissociation pressures of compounds (InAs, InP, and GaP) at their melting point by experimenting with liquid zone compositions above and below stoichiometry. Nashel'skii and coworkers[117] determined the effective partition coefficients of zinc and tin impurities during crystallisation of indium phosphide.

Replenishment of a non-stoichiometric melt in the course of crystallisation from a condensed phase refers to the introduction of crystals of the same compound into the melt. Essentially, this procedure is not so much a method of synthesis as a method of recrystallisation for the purpose of purification, heavy doping, or single crystal preparation. Replenishment of the melt by crystals of the desired compound is a "more powerful" method, to use technological jargon, since it minimises the difference in composition between the crystals entering and those leaving the melt.

Fig. 8 shows Trumbore's method[118] of preparing single crystals of semiconducting compounds from a non-stoichiometric melt replenished from a condensed phase. The melt for growing gallium phosphide was kept at 700–800°, and produced aggregates of small crystals. Gallium arsenide crystals were also grown by this method.

As an alternative to adding feed crystals, a non-stoichiometric melt can be kept at constant composition during crystallisation by removing the excess of one of the components (the more volatile) by evaporation. As an example we may quote the work of Lorenz[119], who prepared cadmium telluride crystals from cadmium-rich (69 at.% Cd) melts. A sealed quartz tube, containing the melt in a

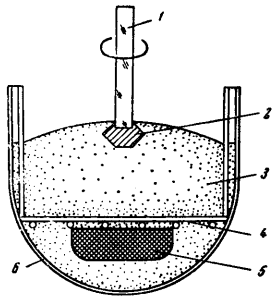


Fig.8. Apparatus for growing crystals of semiconducting compounds from non-stoichiometric melts, with replenishment from a condensed phase:
1) seed rod; 2) growing crystal;
3) gallium–gallium phosphide melt;
4) quartz mesh; 5) feed crystal;
6) quartz crucible.

graphite boat (125 mm), was pulled through a two-zone furnace. As the boat was gradually transferred from the zone at 970° to the zone at 1026° at 1.2 mm h^{-1}, some cadmium evaporated, producing a polycrystalline crop of cadmium telluride. The cadmium vapour was condensed in a zone at 953° (cadmium vapour pressure = 5.9 atm).

6. GENERAL EVALUATION OF THE METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

This review of the preparative methods for semiconducting compounds is arranged in accordance with the classification suggested in Section 2. Individual subgroups have been illustrated by reference to the most typical examples, chosen from the numerous methods described in the literature.

Some of the subdivisions of this classification are arbitrary, and were introduced only because of the distinctive design features of the apparatus employed. For example, there is no real difference in principle between zone melting and normal directional crystallisation with replenishment by a condensed phase, as applied to the preparation of decomposable crystals from their non-stoichiometric melts. When the compound is crystallised from a non-stoichiometric melt containing an excess of the more volatile component, the method becomes a simple one-temperature procedure, and is carried out without controlling the pressure over the melt.

No clear demarcation can be made between methods for preparing compounds without control of the partial pressure of components over the melt but under a pressure of inert gas, on the one hand, and methods of preparation of compounds using a balancing pressure to suppress the diffusion of the more volatile component through a vent, on the other hand. It is also difficult to assign to any particular subdivision of the classification, Stone's novel method[120] for preparing epitaxial gallium phosphide films on gallium arsenide substrates, by diffusional replacement of arsenic by phosphorus atoms. This process was carried out in quartz ampoules in which a phosphorus vapour pressure of 15–20 atm was maintained with a substrate temperature of 800–900°. Technologically, the process is not very different from sintering, but it is essentially an indirect method.

Other methods having a great deal in common are crystallisation from solution in a "third" component and synthesis by condensation in an inert gas stream, synthesis in a stream of one of the components and crystallisation from a non-stoichiometric melt, and so on.

The terminology used to describe the methods of preparation of semiconducting compounds was adopted from the original sources whenever possible, but in many cases we had to resort to literal translation. Therefore, some of the terms used may be slightly unfortunate, but they can undoubtedly be improved by discussion.

To complete this survey of the methods of preparation of semiconducting compounds, it may not be out of place to mention some new methods which, though theoretically possible, have not yet been put to experimental test.

First of all, floating-zone melting (vertical variant) methods are very difficult to apply in practice to semiconducting compounds, on account of their low surface tension and high density. Yet, floating-zone techniques with electromagnetic levitation, "caged"-zone melting[63], and other similar procedures have already been developed for germanium, silicon, and some high-melting metals. Measured such as these should make it possible to apply vertical floating-zone melting to the crucible-free synthesis, purification, and single-crystal growth of compounds, particularly thermally stable ones.

There are no reported instances of the growth of decomposable semiconducting compounds from molten salt solutions. It should be possible, for example, to use the halides of the appropriate metals, or other melts, to prepare solutions of the arsenides and phosphides of Group III (second subgroup) elements, and of the sulphides, selenides, and tellurides of Group II (second subgroup) elements.

The use of a balancing pressure to support the wall of the reaction tube has not been widely applied, as a design feature, to the numerous methods of directional crystallisation from stoichiometric and non-stoichiometric melts. In general, balancing pressure could advantageously be used in all crystallisation methods of preparation of compounds having high dissociation pressures on melting.

Unfortunately, no horizontal methods for growing crystals of compounds from the melt have been developed. These would offer important advantages from the point of view of the removal of impurities from the crystallisation front.

Semiconductor technology is making increasingly stringent demands of chemists and metallurgists for the preparation of semiconducting compounds of higher purity and specified properties. We can therefore expect to witness very rapid developments in semiconductor metallurgy — the science of the preparation of semiconducting compounds — in the near future. The methods and apparatus needed to satisfy the demands of contemporary semiconductor technology will result from the cooperation between research and production staff and academics, engineers, and apparatus designers and fitters.

1. O.G.Folberth, "Halbleiterprobleme", Vol.5, 1960, pp.40–74.
2. C.Hilsum and A.C.Rose-Innes, "Semiconducting III–V Compounds", Pergamon Press, London, 1961.

3. N.B.Hannay (Editor), "Semiconductors", Chapman and Hall, London, 1959.
4. W.D.Lawson and S.Nielsen, "Preparation of Single Crystals", Butterworth, London, 1958.
5. W.G.Pfann, "Zone Melting", Wiley, New York, 1958.
6. N.Parr, "Zone-Refining and Allied Techniques", Chapman and Hall, London, 1960.
7. H.C.Gatos (Editor), "Properties of Elemental and Compound Semiconductors", Interscience (Met.Soc.Conf., Vol.V), New York, 1960.
8. R.O.Grubel (Editor), "Metallurgy of Elemental and Compound Semiconductors", Interscience (Met.Soc.Conf., Vol.XII), New York, 1961.
9. Symposium "Voprosy Teorii i Issledovaniya Poluprovodnikov i Protsessov Poluprovodnikovoi Metallurgii, Materialy Soveshchaniya po Poluprovodnikovym Materialam" (Theoretical and Practical Problems in Semiconductors and Semiconductor Metallurgical Processes, Proceedings of the Conference on Semiconducting Materials), Izd.Akad.Nauk SSSR, Moscow, 1955.
10. Symposium "Voprosy Metallurgii i Fiziki Poluprovodnikov, Trudy 2-go Soveshchaniya po Poluprovodnikovym Materialam" (Problems in the Metallurgy and Physics of Semiconductors, Proceedings of the Second Conference on Semiconducting Materials), Izd.Akad.Nauk SSSR, Moscow, 1957; "Trudy 3-go Soveshchaniya" (Proceedings of the Third Conference), 1959; "Trudy 4-go Soveshchaniya" (Proceedings of the Fourth Conference), 1961.
11. Symposium "Rost Kristallov" (Crystal Growth), Inst.Kristallografii Akad.Nauk SSSR, Izd.Akad.Nauk SSSR, Vol.1, 1957; Vol.2, 1959; Vol.3, 1961.
12. Symposium "Nauchnye Trudy Giredmeta (Raboty 1959 Goda)" (Scientific Publications of the State Research and Development Institute of the Rare Metals Industry, Papers Published in 1959), Vol.6, Metallurgizdat, Moscow, 1962.
13. Symposium "Trudy Instituta Metallurgii Imeni A.A.Baikova Akademii Nauk SSSR" (Transactions of the Baikov Metallurgical Institute of the Academy of Sciences of the USSR), Vol.5, Izd.Akad.Nauk SSSR, Moscow, 1960.
14. "Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Poluprovodnikovym Soedineniyam" (Abstracts of Papers Presented to the All-Union Conference on Semiconducting Compounds), Izd.Akad.Nauk SSSR, Leningrad, 1961.
15. N.A.Goryunova, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 5, 522 (1960).
16. A.S.Borshchevskii, Candidate's Thesis, Kalinin Leningrad Polytechnic Institute, Leningard, 1962.
17. V.P.Zhuze (Editor), "Nauchnaya Literatura po Poluprovodnikam" (Scientific Literature on Semiconductors), Izd.Akad. Nauk SSSR, 1955.
18. V.P.Zhuze (Editor), "Nauchnaya Literatura po Poluprovodnikovym Priboram" (Scientific Literature on Semiconductor Devices), Izd.Akad.Nauk SSSR, 1959.
19. E.Montignie, Bull.Soc.chim.France, 276 (1946).
20. G.R.Antell and O.Effer, J.Electrochem.Soc., 106, 505 (1959).
21. D.Effer and G.R.Antell, J.Electrochem.Soc., 107, 252 (1960).
22. A.Addamiano, J.Amer.Chem.Soc., 82, 1537 (1960).
23. R.Frerichs, Phys.Rev., 72, 594 (1947).
24. M.Gershenzon and R.M.Mikulyak, J.Electrochem.Soc., 108, 148 (1961).
25. G.V.Samsonov, L.L.Vereikina, and Yu.B.Titkov, Zhur. Prikl.Khim., 35, 242 (1962).
26. B.J.Lewis, J.Electrochem.Soc., 109, 497 (1962).
27. A.Addamiano, J.Electrochem.Soc., 108, 1072 (1961).
28. R.Didchenko, U.S.P. 3 010 792 (31st August 1959); Official Gazette, 772, 1099 (1961).
29. I.M.Tsymbalov and T.N.Trushina, USSR P. 143 023; Byull.Izobretenii, 12, No.23, 23 (1961).
30. B.V.Mill' and I.I.Naumova, Kristallografiya, 6, 800 (1961).
31. T.Renner, Z.anorg.Chem., 298, 22 (1959).
32. R.C.Ellis, see Ref.8, p.443.
33. B.E.Bishop and S.H.Liebson, J.Appl.Phys., 24, 660 (1953).
34. E.Scharowsky, Z.Physik, 135, 318 (1953).
35. N.A.Goryunova, N.N.Fedorova, and V.I.Sokolova, Zhur. Tekh.Fiz., 28, 1672 (1958).
36. B.J.Watson, British Communications and Electronics, 9 (9), 448 (1962); Electronics News, 7, No.310, 61 (1962).
37. D.C.Reynolds and S.J.Czyzak, Phys.Rev., 79, 543 (1950).
38. S.J.Czyzak, D.J.Graig, C.E.McCain, and D.C.Reynolds, J.Appl.Phys., 23, 932 (1952).
39. A.Kremheller, Sylvania Technologist, 8, 11 (1955).
40. J.A.Lely, Ber.deut.keram.Ges., 32, 229 (1955).
41. D.R.Hamilton, J.Electrochem.Soc., 105, 735 (1958).
42. K.M.Hergenrother, S.E.Mayer, and A.I.Mlavsky, *ibid.*, pp.60–65 [wrong reference ? (Ed. of Translation)].
43. H.Schafer, "Chemische Transportreaktionen" (Chemical Transport Reactions), Contributions to Angew.Chem. and "Chemie–Ingenieur–Technik", No.76, Verlag Chemie, Weinheim–Bergstr., 1962.
44. N.Holonyak, D.C.Jellison, and S.F.Bevacqua, in "Metallurgy of Semiconductor Materials" (Edited by J.B.Schroeder), Interscience (Met.Soc.Conf., Vol.XV), New York, 1962, pp.49–59.
45. G.R.Antell, Brit.J.Appl.Phys., 12, 687 (1961).
46. A.S.Roy, J.Electrochem.Soc., 109, 750 (1962).
47. T.Ikada and T.Kano, J.Phys.Soc.Japan, 16, 2591 (1961).
48. R.L.Newman and N.Goldsmith, J.Electrochem.Soc., 108, 1127 (1961).
49. P.V.Usachev, A.V.Golubkov, and N.S.Volosatova, Zhur. Prikl.Khim., 33, 2771 (1960).
50. N.V.Kolomoets and E.A.Popova, Fiz.Tverdogo Tela, 2, 1951 (1960).
51. D.Hazelby and J.L.Parmee, J.Electrochem.Soc., 107, 144 (1960).
52. W.D.Lawson, J.Appl.Phys., 22, 144 (1951).
53. T.C.Harman, Quarterly Progress Reports on Solid State Research, Lincoln Laboratory, Massachusetts Institute of Technology, October, 1959, pp.30–32.
54. J.Blear and R.Newnham, see Ref.8, pp.393–402.
55. V.D.Kuznetsov, "Kristally i Kristallizatsiya" (Crystals and Crystallisation), Gostekhteoretizdat, Moscow, 1954
56. K.F.Hulme and J.B.Mullin, Solid-State Electronics, 5, 211 (1962).
57 R.Gremmelmaier and O.Madelung, Naturforsch., 8a, 333 (1953).
58. M.S.Mirgalovskaya and L.I.Matkova, Zhur.Neorg.Khim., 5, 1551 (1960) [Russ.J.Inorg.Chem., 750 (1960)].
59. W.P.Allred, B.Paris, and M.Genser, J.Electrochem.Soc., 105, 93 (1958).
60. H.A.Schell, Z.Metallk., 46, 58 (1955).
61. W.P.Allred, W.I.Mefferd, and R.K.Willardson, J.Electrochem.Soc., 107, 117 (1960).
62. M.S.Mirgalovskaya and I.A.Strel'nikova, Fiz.Tverdogo Tela, 3, 456 (1961).
63. A.Ya.Nashel'skii and V.N.Vigdorovich, "Poluchenie Poluprovodnikov i Metallov Vysokoi Chistoty Metodom Zonnoi Plavki (Obzor Zarubezhnoi Literatury)" [Preparation of Semiconductors and Metals in a High State of Purity (A Survey of Foreign Literature)], GOSINTI, Moscow, 1962.
64. W.G.Pfann, Trans.AIME, 194, 747 (1952).
65. K.J.Hulme and J.B.Mullin, J.Electronics and Control, 3, 160 (1957).
66. J.B.Mullin and K.J.Hulme, J.Electronics, 4, 170 (1958).
67. K.I.Vinogradova, V.V.Galavanov, and D.N.Nasledov, Zhur. Tekh.Fiz., 27, 1976 (1957).
68. K.Shirous, Czech.J.Phys., 6, 39 (1956).

69. H.Welker and H.Weiss, Solid State Phys., 3, 1 (1956).
70. D.F.Edwards and G.S.Hayne, J.Opt.Soc.Amer., 49, 414 (1959).
71. H.A.Schell, Z.Metallk., 49, 140 (1958).
72. F.H.Reid and H.K.Willardson, J.Electronics and Control, 5, 54 (1958).
73. A.Regel' and M.S.Sosninskii, Zhur.Tekh.Fiz., 25, 768 (1955).
74. F.K.Heumann, J.Electrochem.Soc., 109, 345 (1962).
75. R.L.Fisner, R.Mazelsky, and W.A.Tiller, J.Appl.Phys., 32 (10), 1833 (1961).
76. A.H.Smith, see Ref.8, pp.431–441.
77. Angew.Chem., 71, No.21 (1959).
78. Ceramic Age, 74, No.3, 43 (1959); Ceramics, II, No.131, 32 (1960).
79. J.R.O'Connor and J.Smiltens (Editors), "Silicon Carbide, A High-Temperature Semiconductor: Proceedings of the Conference at Boston, Mass., 2–3rd April 1959", Pergamon, London, 1960.
80. F.A.Halden, *ibid.*, pp.115–122.
81. R.C.Ellis, *ibid.*, pp.124–129.
82. A.Landelli, Gazzetta, 71, 58 (1941).
83. R.M.Evans and B.I.Jaffe, Trans.AIME, 194, 153 (1952).
84. T.S.Liu and E.A.Peretty, Trans.ASM, 45, 677 (1953).
85. W.Köster and W.Ulrich, Z.Metallk., 49, 361 (1958).
86. A.S.Borshchevskii and D.N.Tret'yakov, Fiz.Tverdogo Tela, 1, 1483 (1959).
87. M.Shafer and K.Weiser, J.Phys.Chem., 61, 1424 (1957).
88. G.Wolff, P.H.Keck, and J.D.Broder, Phys.Rev., 94, 753 (1954).
89. A.A.Shternberg, I.P.Kuz'mina, and V.A.Kuznetsov, Kristallografiya, 7, 334 (1962).
90. F.Gans, J.Lagrenaudie, and P.Seguin, Compt.rend., 237, 310 (1953).
91. V.N.Vigdorovich and A.Ya.Nashel'skii, Dokl.Akad.Nauk SSSR, 144, 182 (1962).
92. J.van der Boomgard and D.Schol, Philips Res.Rep., 12, 127 (1957).
93. L.I.Marina, A.Ya.Nashel'skii, V.N.Vigdorovich, and D.D.Bakanova, Zhur.Fiz.Khim., 38, 551 (1964) [Russ.J. Phys.Chem., 296 (1964)].
94. T.C.Harman, H.Goering, and A.Beer, Phys.Rev., 104, 1562 (1956).
95. R.Harada and A.Straust, J.Appl.Phys., 30, 121 (1959).
96. F.A.Cunnell, J.T.Edmond, and N.R.Harding, Solid State Electronics, 1, 97 (1960).
97. L.R.Weisberg, F.D.Rosi, and P.G.Herkart, see Ref.7, pp.25–66.
98. R.Gremmelmaier, Naturforsch., 11a, 511 (1956).
99. J.L.Richards, J.Sci.Instr., 34, 289 (1957).
100. P.L.Moody and C.Kolm, Rev.Sci.Instr., 29, 1144 (1958); see also U.S.P. 2 990 259 (27th June 1961).
101. R.Wickham, J.Sci.Instr., 38, 396 (1961).
102. R.Henkel, Electronics News, No.318 (14th May), 1, 62 (1962).
103. J.van der Boomgard, F.A.Kroger, and H.J.Vink, J.Electronics, 1, 121 (1955).
104. D.Effer, J.Electrochem.Soc., 108, 357 (1961).
105. J.L.Richards, J.Appl.Phys., 31, 601 (1960).
106. J.M.Whelan and C.H.Wheatley, Phys.and Chem.Solids, 6, 169 (1958).
107. F.A.Cunnell and R.Wickham, J.Sci.Instr., 37, 410 (1960).
108. C.J.Frosch and L.Derick, J.Electrochem.Soc., 108, 251 (1961).
109. A.Fischer, Naturforsch., 13a, 105 (1958).
110. T.C.Harman, J.I.Genko, W.P.Allred, and H.L.Goering, J.Electrochem.Soc., 105 (11), 731 (1958).
111. A.Ya.Nashel'skii and V.Z.Ostrovskaya, "Nauchnye Trudy Giredmeta (Raboty 1959 Goda)" (Scientific Publications of the State Research and Development Institute of the Rare Metals Industry, Papers Published in 1959), Vol.6, Metallurgizdat, Moscow, 1962, p.201.
112. R.I.Guire and K.Weiser, U.S.P. 2 871 100; Official Gazette U.S.P.Office 27/1, 4, 1132 (1959).
113. E.P.Strambaugh, J.F.Miller, and R.C.Himes, see Ref.8, p.317.
114. L.J.Vieland and S.Skalski, see Ref.8, p.303.
115. R.E.Davis, see Ref.7, p.295.
116. O.G.Folberth, Phys.and Chem.Solids, 7, 295 (1958).
117. A.Ya.Nashel'skii, V.Z.Ostrovskaya, E.M.Burdynskaya, and G.V.Zimina, "Nauchnye Trudy Giredmeta (Raboty 1959 Goda)" (Scientific Publications of the State Research and Development Institute of the Rare Metals Industry, Papers Published in 1959), Vol.6, Metallurgizdat, Moscow, 1962, p.194.
118. F.A.Trumbore, see Ref.8, p.15.
119. M.R.Lorenz, J.Appl.Phys., 33, 3304 (1962).
120. L.E.Stone, J.Appl.Phys., 33, 2795 (1962).

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