METHOD FOR PRODUCING HOMOGENEOUS CRYSTALS OF MIXED SEMICONDUCTIVE MATERIALS

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Fig. 1.

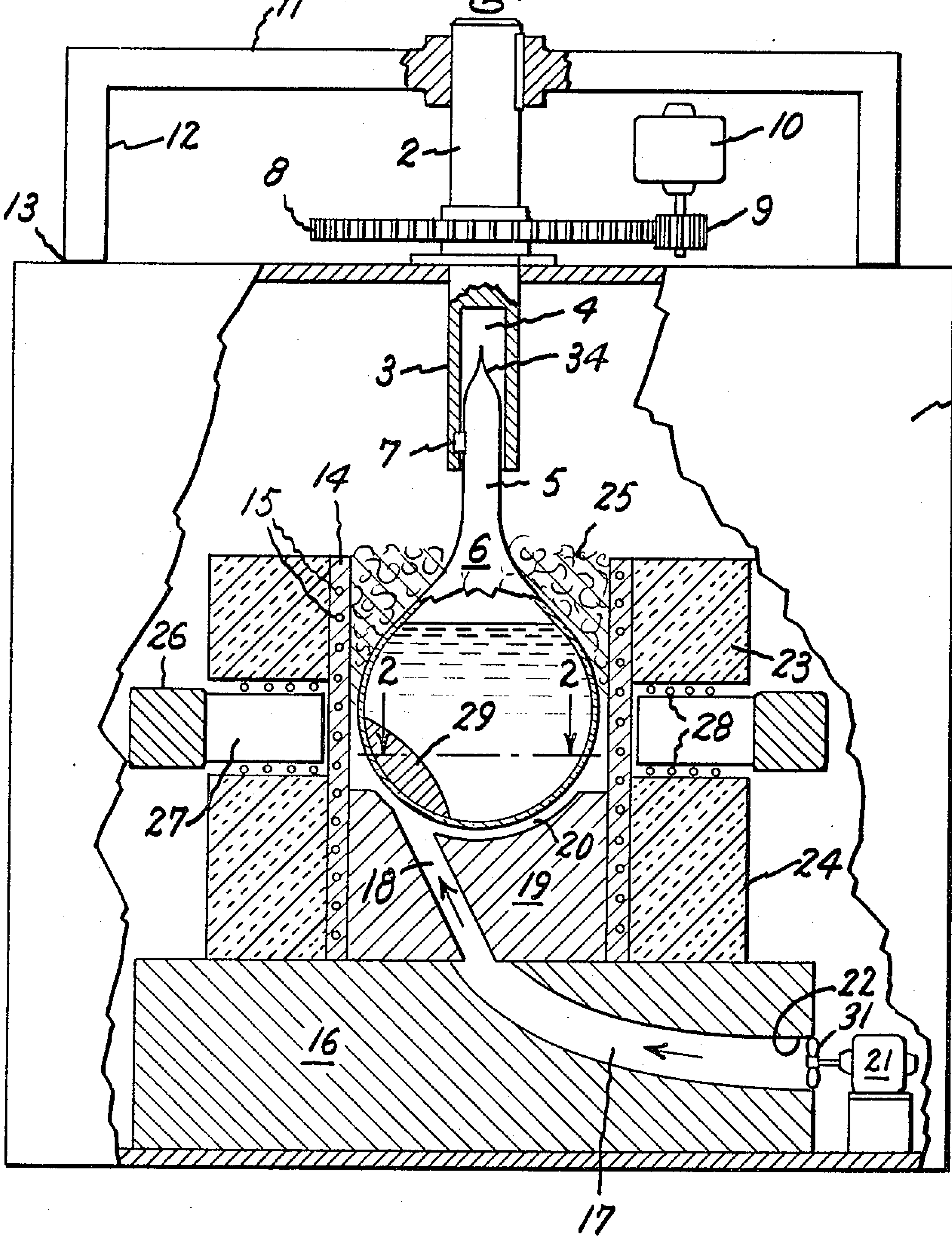


Fig. 2.

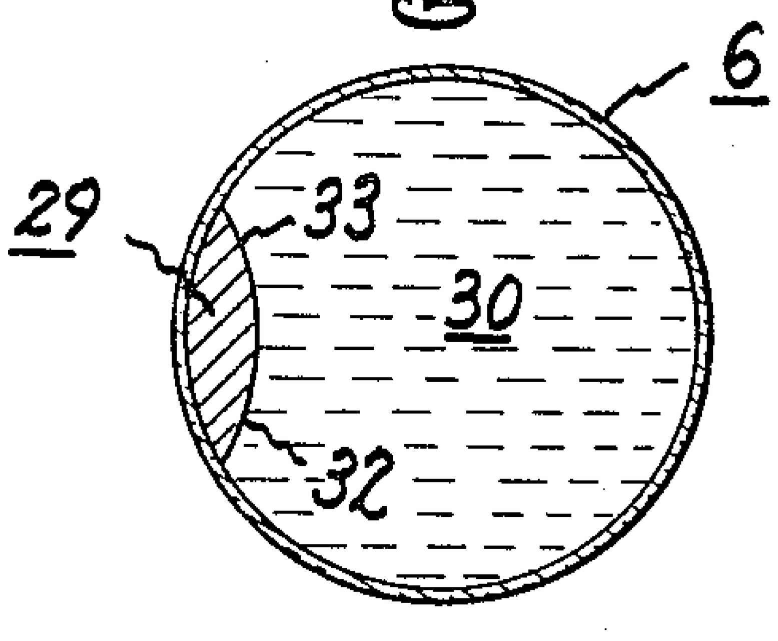
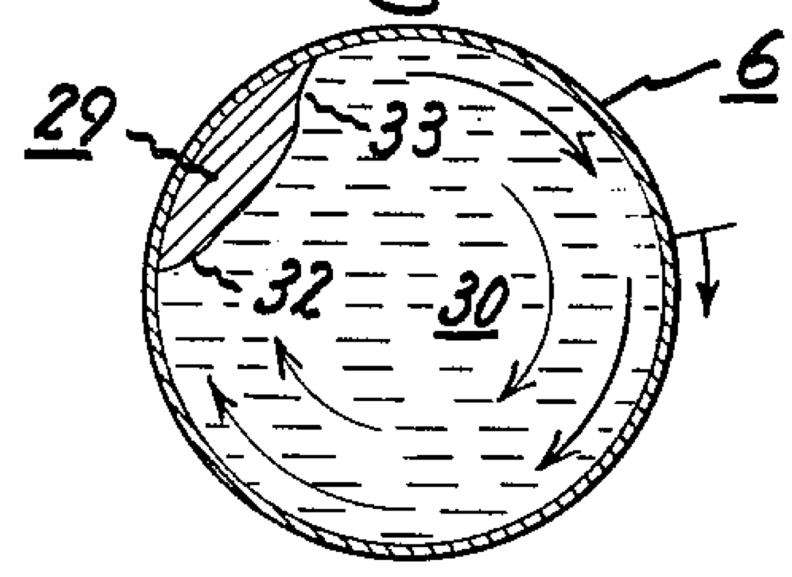


Fig. 3.



Inventor:
Robert N. Hall,
by John F. Ahern
His Attorney.

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METHOD FOR PRODUCING HOMOGENEOUS CRYSTALS OF MIXED SEMICONDUCTIVE MATERIALS

Robert N. Hall, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York

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This invention relates to the production of homogeneous crystals of mixed, mutually soluble, semiconductive materials.

In many applications of semiconductive materials, for example in transistors, lasers and the like it is frequently highly desirable to provide homogeneous crystals consisting essentially of a plurality of mixed semiconductive materials. In this way, the resultant crystal selectively exhibits certain desirable characteristics of the individual constituents to an extent that is controllable, as by regulating the relative proportions of the constituents in the resultant crystal. Many characteristics of the resultant crystal can be controlled to selectively fall within a range defined by the extremes of two or more constituents considered individually. Thus, a given characteristic is selected from a continuous range of optimize performance of the resultant semiconductive crystal in a given application, rather than resort to selection from the discrete group of characteristics offered by individual semiconductive materials.

A serious limitation upon the use of crystals of mixed semiconductive materials has heretofore existed because the mixed crystals obtained contain considerable concentration gradients, or are nonhomogeneous. Oftentimes the relative proportions of constituents vary within the crystal in a random and unpredictable pattern. Such lack of homogeneity impairs the reproductibility of observed phenomena with a given mixed crystal and renders the manufacturing cost of devices employing such crystals prohibitorily high because of the low and uncertain useful yield of marketable devices.

Accordingly, it is an object of my invention to provide a method for producing homogeneous crystals of mixed semiconductive materials.

Another object of my invention is to provide an efficient and economical process for growing and refining homogeneous crystals of mixed, mutually soluble, semiconductive materials.

Yet another object of my invention is to provide apparatus and process for efficiently and effectively producing homogeneous crystals of mixed semiconductive materials and conductivity-determining impurities wherein the relative concentrations of constituents are accurately and precisely controlled.

Briefly, in accord with one embodiment of my invention, the constituents desired in a homogeneous crystal are sealed in a flask and reacted by heating to a temperature at which the mixture is in the liquid phase. The constituents are then cooled in a furnace having a transverse thermal gradient until deposition of a solid occurs on the cooler side of the flask. The flask is thereafter continuously and slowly rotated, while maintaining the average furnace temperature constant, causing one end of the deposit to be dissolved and the other end to be the site of crystalline redeposition. The deposit is "digested" in this manner several times, until the liquid and solid phases reach their respective steady-state equilibrium conditions and thereafter continued until a crystal of the desired degree of homogeneity is obtained.

The features of my invention that I believe to be novel are set forth with particularity in the appended claims. My invention, however, both as to its organization and

method of operation, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the accompanying drawing in which:

FIGURE 1 is a cross-sectional view of apparatus suitable for use in the practice of my invention;

FIGURE 2 is a sectional top view of the flask in the apparatus of FIGURE 1; and

FIGURE 3 is a view as in FIGURE 2, but schematically showing operation of the process.

The apparatus of FIGURES 1 and 2 comprises an outer support and housing **1** having a shaft **2** positioned vertically and journaled in the top of housing **1** for rotation about its vertical axis. The lower portion of shaft **2**, that projects into housing **1**, includes an end portion **3** thereof having a concentric annular recess **4** formed therein that is adapted to receive and closely surround the neck portion **5** of a flask, or reaction vessel **6**. Vessel **6** is conveniently made of a suitable inert refractory material, as for example, quartz, aluminum nitride, or carbon.

A fastening device **7** is carried by the lower portion **3** of shaft **2** and projects inwardly into recess **4** to securely fix neck portion **5** with respect to shaft **2**. When vessel **6** is fabricated from fused quartz, fastening device **7** also may be formed, conveniently, from fused quartz.

A ring gear **8** is securely fastened to shaft **2** externally of enclosure **1**. Gear **8** is engaged by drive gear **9** that is turned by motor **10** to effect rotation of shaft **2** and vessel **6** that is secured thereto by fastening device **7**. Additional vertical support for shaft **2** is provided by spider **11** that is secured to the upper extremity of shaft **2** and includes legs **12** that bear down upon the top surface of housing **1** along circular surface **13**.

Heating means for the contents of vessel **6** include a thin walled cylinder **14** closely surrounding the outer periphery of vessel **6** and having imbedded therein a helical winding comprising a plurality of turns of resistance wire **15**. Cylinder **14** is fabricated from a refractory insulating material and is supported atop a lower platform **16** that in turn rests upon the inner floor of housing **1**. Support **16** includes a duct **17** that communicates with a passage **18** formed in an otherwise solid cylindrical member **19** that fits tightly within cylinder **14** and includes an upper surface **20** that is shaped to receive the lower portion of vessel **6**. Means for circulating the atmosphere within housing **1** into duct **17** is illustrated schematically as including a motor **21** driving a fan blade **31** disposed near the entrance **22** of duct **17**. The cooling atmosphere is directed by passage **18** toward one peripheral segment of vessel **6**.

The efficiency of the heating means is increased by providing annular insulating blocks **23** and **24**, conveniently made from refractory heat insulating material, externally of and closely surrounding cylinder **14**. Further means for increasing the efficiency of the heating means includes a bat of refractory insulating material **25** inside cylinder **14** and covering the top of vessel **6**. The insulating material is, conveniently, quartz wool, in order to provide the required porosity to release the cooling atmosphere delivered from passage **18**.

Preferably, stirring means is provided and takes the form of an annular yoke **26** having integral pole pieces **27** extending inwardly therefrom and terminating adjacent the outer periphery of cylinder **14** and in vertical alignment with the largest diameter portion of vessel **6**. A plurality of turns **28** of electrically conducting, insulated wire on each of poles **26** comprise the electric circuit necessary to cause a magnetomotive force sufficient to establish magnetic flux linking the various poles and including as a portion of the path the contents of vessel **6**. Yoke **26** can, for example, take the form of a conventional induction motor stator and electrical connections sufficient to provide a revolving magnetic field in the vicinity of vessel **6** are well-known and can be obtained easily from most text books which treat the subject of alternating current machinery.

My invention is used to greatest advantage for growing and refining homogeneous mixed semiconductive crystals having concentrations of constituents differing appreciably from the concentrations of constituents in the melt from which the crystal is grown. For this reason, my invention is particularly useful for providing mixed, or solid solution, homogeneous semiconductive crystals in various systems including, indium antimonide-gallium antimonide, indium antimonide-aluminum antimonide, gallium antimonide-aluminum antimonide, indium arsenide-gallium arsenide, indium arsenide-indium phosphide, and gallium arsenide-gallium phosphide. My invention is also advantageously employed to grow and refine various mixed semiconductive crystals from the II–VI compounds, as for example, cadmium telluride-cadmium sulfide, zinc telluride-zinc sulfide. Other systems include germanium-silicon crystals grown from a solution of tin or gold having germanium and silicon introduced therein, or quaternary solid solution systems such as gallium-indium-arsenic-phosphorus and gallium-indium-arsenic-antimony. In the interest of brevity and clarity, the ensuing description will be confined to the mixed semiconductive crystal system consisting essentially of gallium arsenide-gallium phosphide, with suitable acceptor or donor impurities therefor in some cases. This system is typical of the complex-compound semiconductive materials produced in homogeneous crystalline form, in accord with my invention.

Within vessel **6** there is enclosed a charge, or mixture of reaction products, that is partially in the liquid phase and partially in the solid phase. For a wide range of temperature distributions within vessel **6**, a portion of a given charge deposits as a solid and another portion is in the liquid state. At equilibrium, the relative concentrations of constituents in the solid and liquid phases correspond to the proportions given by what is known in the art as a "phase diagram" of the system.

The above described heating means, for heating the charge within vessel **6**, is adapted to establish within the charge a temperature distribution with a transverse thermal gradient such that substantially all, and preferably greater than 80 percent, of the charge is in the liquid phase in order to encourage homogeneity and thorough mixing of the liquid constituents. Also, the heating means is preferably adapted to establish a temperature gradient having a coolest temperature adjacent one peripheral segment of vessel **6**, in order to promote deposition of the solid portion and growth of a crystal thereat. Freezing of the latter portion occurs to a solid state body, represented as crystalline body **29** shown growing on the side of one peripheral segment of vessel **6** that is the coolest segment, due to the cooling atmosphere from passage **18**.

When the constituents of crystal **29** are to be gallium arsenide and gallium phosphide, for example, the charge is selected to contain a predominant concentration of gallium that serves as a solvent into which arsenic and phosphorus are introduced and, preferably, the upper extremity, or tip **34**, of neck portion **5** of vessel **6** is sealed. Alternatively, phosphorus and arsenic can be introduced, as gaseous reaction partners, continuously during the growing and refining process into a solvent of gallium by providing a suitable gaseous carrier therefor such as hydrogen or argon.

FIGURES 2 and 3, which are horizontal cross-sectional views of vessel **6** of FIGURE 1 taken along section lines **2—2**, illustrate the method of operation of the specific apparatus shown in FIGURE 1. When the heating means has been energized for sufficient time to establish the temperature gradient described above, a deposit of the same materials as the molten mass is formed on the peripheral segment of vessel **6** wherein the lower temperature is maintained. The remainder of the charge **30** is in the liquid state.

In accord with one aspect of my invention, seed crystal **29** is continuously displaced relative to the heating means, as by continuous rotation of vessel **6** about its vertical axis by motor **10**, as seen in FIGURE 1. When the displacement of crystalline body **29** is clockwise, relative to the heating means, as shown more particularly in FIGURE 3, there is simultaneously established a freezing interface **32** and melting interface **33** in body **29** at respective opposite ends thereof.

With any fixed displacement of body **29** relative to the heating means, the melting and freezing occurs until body **29** achieves the same equilibrium position (shown in FIGURE 2) relative to the heating means that it occupied prior to the displacement. Thus, body **29** may be considered to creep around the peripheral surface of vessel **6** in the direction opposite to small angular displacements thereof, about a vertical axis, relative to the heating means. Of course, when body **29** is rotated counterclockwise, relative to the heating means, the freezing and melting interfaces reverse positions at the ends of body **29** to effect the described movement of body **29** back to the equilibrium position.

In accord with a preferred embodiment of my invention the crystalline body is continually displaced relative to the heating means, as by means of motor **10** in FIGURE 1, that is adapted to provide continuous rotation of vessel **6** relative to the heating means. As mentioned above, the particular direction of rotation selected is immaterial, and, of course, in some applications it is equally advantageous to rotate the heating means while maintaining the reaction vessel in a fixed position. By providing continuous displacement, continuous melting of body **29** back into the liquid phase occurs at one end of body **29** and continuous freezing, or recrystallization, occurs at the other end. In this way, body **29** is continuously dissolved and recrystallized, or "digested," until a crystal of the desired homogeneity is obtained.

Circulation, or stirring, of the portion of the charge that is in the liquid phase is advantageously used to accelerate diffusion within the liquid phase to promote a more uniform concentration, resulting in increased homogeneity within body **29**, and permitting more rapid growth. Preferably, the circulation, or rotation, is in the direction from the melting interface to the freezing interface, as shown in FIGURE 3, in order to provide maximum opportunity for diffusion, since the longitudinal dimension of body **29** is normally small relative to, and usually less than ¼, the circumference of vessel **6** at that section wherein crystal growth occurs. A further effect of rotating the liquefied portion of charge **30** is to shift the equilibrium position of crystal **29**, relative to the heating means, by a predetermined fixed angular displacement that is in the same direction as rotation.

By way of specific illustration only, and not to be construed in a limiting sense, a homogeneous crystal constituted of 35 mol percent gallium phosphide remainder essentially gallium arsenide, having a donor concentration of 10^{18} cm.$^{-3}$ is produced as follows. A charge constituted of 42.8 grams gallium, 6.27 grams arsenic, 0.915 gram phosphorus, and 0.024 gram tellurium (donor impurity) is provided in a quartz flask, as shown in FIGURE 1, having a bulb diameter of 1¼ inches. The flask is then sealed in an inert atmosphere and heated to a temperature of about 1050° C. to react the constituents. Then a peripheral segment of the flask is slightly cooled to promote deposition of the crystalline solid thereat and the flask is rotated at ¼ revolution per day for 8 days. The resultant homogeneous, N-type conductivity, gallium arsenide-gallium phosphide crystal is recovered after cooling by fracturing the flask.

It has been found that the most desirable flask rotation rates fall within the range of from ½ to ⅛ revolution per day with flasks of the above-mentioned bulb diameter. Of course, the rate is advantageously selected to be less with larger diameter flasks and vice versa. The duration of time during which the process is carried out varies directly with the desired degree of homogeneity required in the crystal.

By way of another specific illustration, a large high purity homogeneous gallium phosphide crystal is produced in accord with my invention as follows: 90 grams of gallium are placed in an open quartz flask, 5 centimeters in diameter, and supported on an insulating slab. Three pole pieces providing a three-phase rotating magnetic field are disposed substantially symmetrically about the outer lower peripheral surface of the flask. Approximate distance between pole pieces is about 2½ inches and each core is about ½ square inch in cross section. The cores each contained 900 turns of conductive wire and the current measured was about 2 amperes, resulting in an electromotive force of approximately 1800 ampere-turns. In the presence of this field the gallium rotated about 20 rounds per minute.

Thereafter, hydrogen is passed over yellow phosphorus that is heated to about 200° C. and into the flask. The gallium is heated locally at one side of the flask by means of a radio frequency coil, bringing the average temperature to about 1030° C. The phosphorus reacts with the gallium as it passes through the flask forming gallium phosphide which at first dissolves in the gallium. Later, when the solution becomes supersaturated, the gallium phosphide deposits on the side of the flask opposite the heater. Rotation of the flask in one direction at approximately 1 revolution per day causes relative motion of the crystal in the opposite direction by continuous melting and recrystallization. The relatively rapid rotation provided by the magnetic field was observed to enhance the crystal growth rate and homogeneity.

By way of further example, a homogeneous crystal consisting essentially of 60 mol percent gallium arsenide, remainder indium arsenide is advantageously produced in accord with the previous example by introducing 30 grams of gallium, 60 grams of indium and 20 grams of arsenic into the flask. However, in this case, the flask is sealed, heated to an average temperature of 760° C. and a rotation of ½ revolution per day continued for 4 days in the presence of the magnetic stirring.

In general, a large single homogeneous crystal constituted of mutually soluable constituents is produced in accord with my invention by a continuous regrowing technique from a supersaturated solution. This is accomplished by slowly rotating the reaction vessel containing the constituents relative to heating means that provides a thermal gradient. Preferably, the melt is rotated, or circulated, but at a much faster rate than the vessel is turned. The crystal is constrained to a substantially constant spatial relationship with respect to the heating means. Continuous regrowth by freezing and melting is continued until equilibrium conditions, with respect to relative concentrations, have been established. This technique is particularly suitable for producing large homogeneous crystals constituted of mixtures of complex semiconductive compounds and readily lends itself to introduction of desired impurities.

While I have shown and described my invention with respect to preferred embodiments thereof, many modifications and variations will readily suggest themselves to those skilled in the art. Therefore, it is intended by the appended claims to include variations and modifications which fall within the true spirit and scope of my invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A process for producing a homogeneous semiconductive crystal constituted essentially of predetermined mutually soluble constituents, which process comprises:

(a) providing in a reaction vessel a charge comprising said constituents;

(b) heating said charge, by heating means, and maintaining therein a temperature distribution consisting of temperatures in excess of the melting temperature of said charge throughout substantially all of said charge except for one portion of said charge in which portion is maintained a lower temperature and in which portion freezing to a solid state body occurs; and

(c) displacing said body relative to said heating means to simultaneously establish, at opposite interfaces of said body with the melted portion of said charge, freezing at one of said interfaces and melting at the other of said interfaces throughout the entire displacement duration.

2. The process of claim **1** including the further step of establishing circulation of the melted portion of said charge.

3. The process of claim **2** wherein the step of displacing said body relative to said heating means comprises rotating said vessel relative to said heating means, said circulation being in the same angular direction as said vessel rotates relative to said heating means.

4. A process for growing and refining a homogeneous mixed semiconductive crystal constituted essentially of predetermined mutually soluble semiconductive constituents, which process comprises:

(a) providing in a reaction vessel a charge constituted of said constituents;

(b) heating said charge, by heating means, and maintaining therein a temperature distribution consisting of temperatures in excess of the melting temperature of said charge throughout substantially all of said charge except for one portion of said charge adjacent a peripheral segment of said vessel in which portion is maintained a lower temperature and in which portion deposition of a solid state crystalline semiconductive body on said segment occurs; and

(c) rotating said vessel relative to said heating means to simultaneously establish, at opposite interfaces of said body with the melted portion of said charge, recrystallization at one of said interfaces and melting at the other of said interfaces throughout the entire duration of rotation.

5. The process of claim **4** including the further step of establishing circulation of the melted portion of said charge.

6. The process of claim **5** wherein said circulation is in the same angular direction as said vessel rotates relative to said heating means.

7. A process for growing and refining a homogeneous mixed semiconductive crystal constituted essentially of predetermined mutually soluble constituents, which process comprises:

(a) providing in a reaction vessel a charge comprising said constituents;

(b) heating said charge, by heating means, and maintaining therein a temperature distribution consisting of temperatures in excess of the melting temperature of said charge throughout substantially all of said charge except for one portion of said charge adjacent a peripheral segment of said vessel in which portion is maintained a lower temperature than said melting temperature and in which portion freezing to a solid state body occurs; and

(c) continuously displacing said body relative to said heating means to concomitantly establish, at opposite interfaces of said body with the melted portion of said charge, continual freezing at one of said interfaces and continual melting at the other of said interfaces.

8. The process of claim **7** including the further step of establishing circulation of the melted portion of said charge.

9. The process of claim 8 wherein the step of continuously displacing said body relative to said heating means comprises rotating said vessel relative to said heating means, said circulation being in the same angular direction as said vessel rotates relative to said heating means.

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TOBIAS E. LEVOW, *Primary Examiner.*

R. D. EDMONDS, *Assistant Examiner.*