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APPARATUS FOR GROWING CRYSTALS

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Fig. 1.

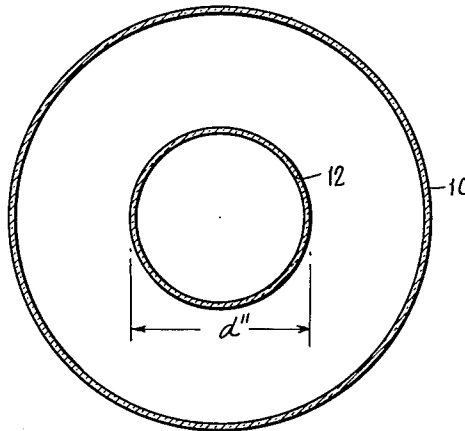
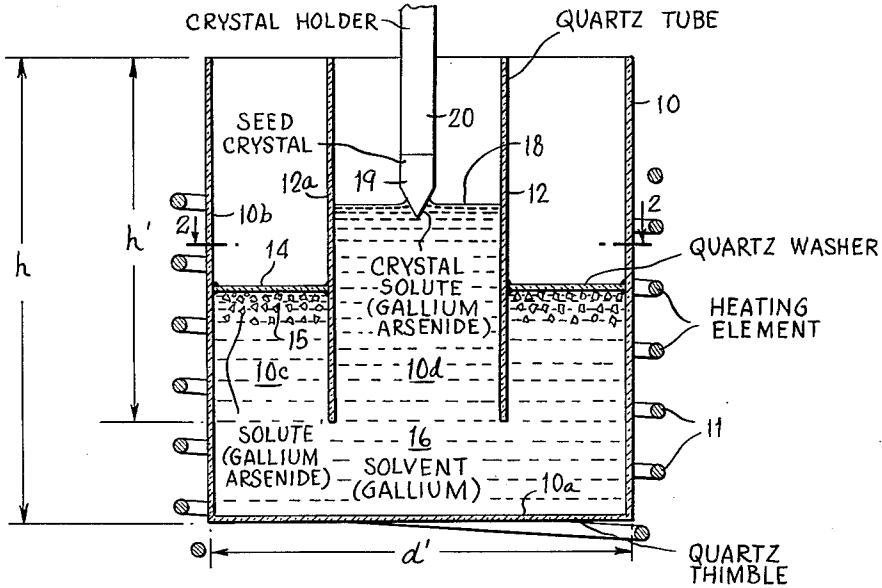


Fig. 2.

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## APPARATUS FOR GROWING CRYSTALS

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1 Claim. (Cl. 23—273)

This invention relates to a method and apparatus for growing crystals. More particularly, this invention relates to a method and apparatus for effecting crystal growth under controlled conditions of temperature and concentration of the crystal-forming material dissolved in a suitable solvent medium. Still more particularly, this invention relates to an improved method and apparatus for growing monocrystals and polycrystals of semiconductive materials.

A major problem usually encountered in crystal growth from solution is the maintenance of a constant solute (material which forms the crystal) concentration in the solution containing the same and from which the crystal is to be grown. Various techniques and apparatus have been suggested and employed for controlling solute concentration in the solution from which the solute material is to be crystallized. None of the methods or apparatus suggested or employed heretofore has been completely satisfactory, especially without requiring careful and continuous control of the crystal growing operation.

It is an object of this invention to provide an improved method and apparatus for effecting crystal growth.

Another object of this invention is to provide a method and apparatus for growing crystals which require relatively little operational control.

Still another object of this invention is to provide apparatus whereby certain crystal growing conditions during the crystal growing operation are controlled due to the nature and structure of the apparatus employed.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawings wherein:

FIG. 1 schematically illustrates in vertical cross-section a crystal growing apparatus in accordance with this invention, as well as indicating the practice of this invention; and

FIG. 2 is a cross sectional view taken along line 2—2 of the apparatus illustrated in FIG. 1.

In accordance with this invention it has now been discovered that an improved method of growing crystal solute from a solution containing said solute dissolved in a suitable solvent is provided by forming a solution of said solute in a body of a suitable solvent, dividing said body of solvent into two portions, a first portion and a second portion, said first portion being in fluid communication with said second portion and the concentration of said solute in said first portion being greater than the concentration of said solute in said second portion, and introducing into contact with said second portion a seed crystal of said solute for growth of crystalline solute thereon. Suitable apparatus for effecting crystal growth in accordance with this invention comprises a container open at the top, an envelope disposed in a substantially upright position within said container, said envelope being open at both ends, the lower end of said envelope being spaced from the bottom of said container and means located in the annulus intermediate said container and said envelope fixing said envelope to said container.

In the practice of this invention for the growth of crystal solute material from a solution containing said solute dissolved therein, said solution is divided into two portions, a first portion and a second portion, said first portion being in open, direct fluid communication with

said second portion. The concentration of solute in said first portion of said solution is maintained higher than the concentration of solute in said second portion of said solution. A seed crystal of solute material upon which crystalline solute is to be deposited is placed into contact with said second portion of said solution under crystal-forming conditions to deposit crystal solute on said seed crystal. As crystalline solute is deposited on or crystallizes on said seed crystal solute material additional solute material, due to the difference in concentration of solute between said first portion and said second portion of said solution, is supplied from said first portion to said second portion. The maintenance of a high concentration of solute material in said first portion of solution relative to said second portion is effected by causing an additional amount of solute to be dissolved therein, desirably in an amount and at a rate equal to the amount and rate at which solute crystal is crystallized from said second portion of said solution onto said seed crystal and/or at which said dissolved solute material moves from said first portion to said second portion of said solution due to the solute concentration differential therebetween.

In accordance with one embodiment of this invention a higher concentration of solute is achieved and maintained in said first portion of said solution as compared with said second portion of said solution by maintaining said first portion of said solution in contact with solid solute material so as to be substantially saturated therewith and, desirably, by maintaining the temperature of said first portion of said solution at a temperature higher than said second portion of said solution. This embodiment of the invention is particularly applicable to the growth of crystalline solute material from a solution in a solvent wherein said solute material evidences increased solubility in said solvent with an increase in temperature. Accordingly, it is thus seen that by maintaining the first portion of said solution at a higher temperature and under conditions such that said first portion of said solution is saturated with solute, the concentration of said solute material in said second portion of said solution tends to be lower, particularly since crystal growth of said solute material occurs in said second portion of said solution thereby continuously removing solute material from solution during the crystal growing operation. Crystal growth is promoted from said second portion of said solution since said second portion of said solution tends to become supersaturated with respect to said solute due to the fact that said second portion of said solution is maintained at a temperature lower than the first portion of said solution.

As indicated hereinabove, said solution containing solute dissolved therein is divided into two portions, a first portion and a second portion, said first and second portions being in direct, fluid communication with each other. In accordance with one embodiment of the practice of this invention said solution is provided within a suitable container, such as a cylindrical container, which is divided into the aforesaid portions by providing within said container a fluid impermeable barrier which effectively seals off and covers a portion of the upper surface of the solution therein, e.g. the surface of said first portion of said solution, said barrier also extending downwardly into said solution only part of the way therinto. That portion of the surface of said solution covered by said barrier and the solution encompassed between the wall of the container and that section of said barrier extending downwardly into said solution comprises the aforesaid first portion of the solution in the practice of this invention. The remaining portion of said solution, i.e. the amount of solution not so encompassed between said fluid impermeable barrier and the peripheral wall of the container comprises essentially the aforesaid second

portion of the solution in the practice of this invention. The top surface or level of said second portion is uncovered by said fluid impermeable barrier and is otherwise available for contact with a seed crystal of the solute material for crystal growth thereon. Since the fluid impermeable barrier extends only part of the way down into said solution within the container, said first and second portions of said solution are in direct communication with each other at the lower section of the container so that during the crystal growing operation dissolved solute material under the influence of the concentration and/or temperature gradient between said first portion and said second portion of said solution moves from said first portion into the second portion of said solution.

Desirably, in the practice of this invention a temperature gradient is maintained between the first portion and the second portion of said solution. A suitable method of maintaining a temperature gradient is to dispose the solution within a container provided with a fluid impermeable barrier therein, said barrier having a form or shape such that said first portion of the solution within the container encompasses or surrounds said second portion and is only in direct communication with said second portion at about the bottom of said first portion so that said first portion and said second portion are only in direct fluid communication with each other at their respective lower portions. In such an arrangement it is possible to maintain the temperature of said first portion substantially different from the temperature of said second portion. For example, upon the application of heat to the outside wall of the container it is possible to maintain the temperature of the first portion of the solution substantially higher than the temperature of the second portion of the solution, the fluid impermeable barrier within said container and dividing said solution into a first portion and a second portion serves to prevent convection currents within said first portion from reaching said second portion and thereby increasing the temperature of said second portion to substantially that of said first portion. It is thus seen that substantially all the heat supplied to said second portion from said first portion passes through the annular body of said first portion of the solution which is substantially isothermal, i.e. all of the first portion of said solution is at substantially the same temperature during the crystal growing operation, and then is conducted through the fluid impermeable barrier into said second portion.

Any suitable temperature differential between said first portion and said second portion effective in the practice of this invention to promote the growth of crystal solute onto the seed crystal of solute material introduced into contact with said second portion of the solution may be employed. Specifically, the temperature differential between said first portion and said second portion may be in the range 10-300 degrees centigrade, more or less, depending upon the physical properties (solubility) of the solute material to be crystallized, the solution, melting points of solute and solvent, the design, size and conformation of the container and the fluid impermeable barrier therein. A temperature differential as low as about 5 degrees centigrade and as high as about 500 degrees centigrade might be employed depending to some extent upon the order of magnitude of the temperature of said first portion of said solution.

As indicated, the practice of this invention is generally applicable to the crystallization of solutes from various solutions containing solute material dissolved therein. Specifically, the practice of this invention is also applicable to the crystallization of solutes, such as chemical compounds, such as salts, e.g. Rochelle Salt, from an aqueous medium or from a non-aqueous medium.

The practice of this invention is particularly applicable to the crystallization of solute material from solutions wherein the solvent is a liquid non-aqueous, metallic medium, e.g. gallium, germanium, indium, tin or suitable

compound thereof, such as indium antimonide, zinc and the like. Solute materials which are suitable for crystallization in accordance with the practice of this invention include the elements such as germanium and such materials or compounds having the formula AB, wherein A is an atom selected from the group consisting of boron, aluminum, gallium and indium and B is an atom selected from the group consisting of nitrogen, phosphorus, arsenic and antimony, specifically, such compounds as indium antimonide, gallium arsenide, indium arsenide, gallium antimonide, gallium phosphide, indium phosphide and the like. In general, any solute material capable of crystallization may be crystallized from a solution in accordance with the practices of this invention, although the invention has particular utility with respect to the growing of monocrystals or semi-conductive materials having substantially constant characteristics over and extended portion of the grown crystal.

Reference is now made to the drawings which schematically illustrate an apparatus suitable for use in the practice of this invention, the drawings also being illustrative of a practice of this invention. Cylindrical container 10, preferably made of quartz, has associated therewith heating element 11, such as an electrical heating element. Container 10 has disposed substantially concentrically therein an open-ended tube 12, preferably cylindrical in shape and preferably made of quartz. As illustrated in FIG. 1 tube 12 extends only part of the way downwardly within container 10 so that the bottom end of tube 12 is spaced from bottom 10a of container 10. The upper end of tube 12 may be conveniently located at about the same level as the top of container 10, although the top of tube 12 may be higher or lower than the top of container 10. Washer 14 is provided within container 10 fixed to the inside wall 10b thereof and to the outside wall 12a of tube 12. Washer 14 is also preferably made of quartz.

In the above arrangement illustrated in FIG. 1 washer 14 fixes tube 12 to container 10. The combination of washer 14 and the lower portion of tube 12, i.e. that portion of tube 12 extending downwardly within container 10 beneath washer 14 serves as a fluid impermeable barrier to divide the interior of container 10 into two sections or portions, an annular, peripheral section or portion 10c and an inner section or portion 10d, said portions 10c and 10d being in direct fluid communication within container 10 at the bottom thereof beneath the bottom end of tube 12.

There is introduced within container 10 solid, particle form, semi-conductive material, e.g. gallium arsenide 15, and a suitable solvent therefor, e.g. liquid gallium 16. Since gallium arsenide 15 is less dense than liquid gallium, it tends to float thereon. The particle form gallium arsenide 15 and the liquid gallium 16 are introduced into container 10 so that all the gallium arsenide is within the annular, peripheral portion of container 10 and liquid gallium completely occupies this portion or so-called first portion 10c of container 10, and no free space is present within first portion 10c of container 10. The liquid gallium thus-introduced within container 10 presents a liquid surface or liquid level 18 within tube 12. Desirably, liquid level 18 is substantially above the level of washer 14 within container 10. It is thus seen that the liquid gallium introduced into container 10 is divided by washer 14 and that section of tube 12 extending downwardly from washer 14 within container 10 into two portions, a first portion completely occupying portion 10c of container 10 and a second portion occupying portion 10d within tube 12.

The liquid gallium 16 in contact with the solid, particle form gallium arsenide 15 within container 10 dissolves at least a portion thereof so that the liquid gallium in portion 10c of container 10 becomes substantially saturated with gallium arsenide. Heat is then applied to the outside of container 10 by means of heating element

11. When heat is applied to container 10 the temperature of the liquid gallium-solid gallium arsenide mixture within portion 10c increases and the gallium arsenide tends to dissolve in the liquid gallium. Since heating element 11 substantially completely surrounds the outside of container 10 the temperature of the resulting liquid gallium solution of gallium arsenide within portion 10c of container 10 tends to increase and to be higher than the temperature of the liquid gallium solution within portion 10d of container 10 within tube 12.

Washer 14 and the lower section of tube 12 extending beneath washer 14 serves as a liquid impermeable barrier and tends to prevent the relatively hot, thermal convection currents generated within the gallium solution in portion 10c of container 10 from reaching the gallium solution within portion 10d of container 10. Substantially all heat transfer from heating element 11 to the gallium solution within portion 10d within tube 12 is effected only through the gallium solution within portion 10c and the wall of tube 12 within container 10 beneath washer 14. It is thus seen that upon the application of heat to container 10 by means of heating element 11 a temperature gradient is built up and maintained within container 10, the gallium solution within portion 10c of container 10 being at a higher temperature than the gallium solution within portion 10d of container 10.

Since gallium arsenide exhibits increased solubility in liquid gallium with an increase in temperature, it is apparent that the concentration of gallium arsenide within the gallium solution in portion 10c is greater than the concentration of gallium arsenide in the gallium solution within portion 10d of container 10. When the gallium solution within portion 10c has reached a suitable temperature, above about 500° C., e.g. in the range 500-900° C., more or less, and a suitable temperature differential, such as a temperature differential above about 25 degrees centigrade, e.g. a temperature differential in the range 25-200 degrees centigrade, has been reached between the main body of the gallium solution within portion 10c of container 10 and the main body of the gallium solution within portion 10d of container 10, a seed crystal of gallium arsenide 19 supported at the lower end of seed crystal holder 20 is introduced beneath liquid level 18 into contact with the gallium solution within portion 10d of container 10 so as to wet the surfaces of seed crystal 19. Desirably, seed crystal 19 of gallium arsenide is then partially withdrawn, now wetted with the gallium solution to, in effect, create a meniscus of gallium solution extending from liquid level 18 upwardly onto the wetted surfaces of gallium arsenide seed crystal 19. The crystal growing operation for the production of crystalline gallium arsenide is then commenced.

During the crystal growing operation crystal holder 20 carrying seed crystal 19 at the bottom thereof is slowly rotated, about 10 r.p.m., while maintaining a portion of seed crystal 19 in contact with the body of gallium solution within portion 10d of container 10 and beneath liquid level 18. Because of the difference in gallium concentration between the gallium solution within portion 10c of container 10 and the gallium solution within portion 10d of container 10 transport of dissolved gallium arsenide from the gallium solution within portion 10c of container 10 to the gallium solution within portion 10d of container 10 occurs. As indicated hereinabove, this difference in gallium arsenide concentration within portions 10c and 10d of container 10 is due to the temperature differential maintained in between portions 10c and 10d of container 10.

Under the gallium arsenide crystal-forming conditions maintained in the gallium solution within portion 10d of container 10, gallium arsenide from the gallium solution crystallizes upon gallium arsenide seed crystal 19. Gallium arsenide crystal growth onto seed crystal 19 occurs upon the wetted surfaces of the gallium arsenide seed crystal 19 and the resulting crystal growth spreads out-

wardly, substantially horizontally from seed crystal 19 within tube 12. At the same time gallium arsenide crystal growth extends from seed crystal 19 downwardly into gallium solution within portion 10d of container 10. Accordingly, gallium arsenide crystal growth occurs, in effect, on seed crystal 19 out of the gallium solution within portion 10d of container 10. As gallium arsenide crystal growth continues on seed crystal 19 the newly-formed crystal surfaces of gallium arsenide on seed crystal 19 become wetted with gallium solution 16 thereby affording additional surface crystal growth thereon. By the above mechanism, gallium arsenide crystal growth on seed crystal 19 proceeds out of the gallium solution in portion 10d of container 10 and outwardly and downwardly from seed crystal 19.

As gallium arsenide crystallization occurs on seed crystal 19, the supply of gallium arsenide in the gallium solution within portion 10d of container 10 is replenished by additional solution of solid gallium arsenide 15 into the gallium solution within portion 10c of container 10. Accordingly, the gallium solution within portion 10c of container 10 is maintained substantially saturated with gallium arsenide. As additional gallium arsenide 15 goes into solution within the gallium solution in portion 10c of container 10, the space previously occupied by this gallium arsenide is occupied by the gallium solution therein. As this occurs, liquid level 18 within tube 12 tends to drop with the result that, in effect, the resulting grown gallium arsenide crystal appears to grow out of the gallium solution within portion 10d of container 10. This growth of gallium arsenide out of the gallium solution and the resulting drop in liquid level 18 of gallium solution 16 within tube 12 is due to the growth of gallium arsenide crystal in a substantially horizontal direction outwardly from seed crystal 19 within portion 10d of container 10.

Growth of gallium arsenide crystal onto seed crystal 19 is continuous until the source of gallium arsenide within portion 10c of container 10 has been substantially completely depleted, i.e. until about substantially all of the solid gallium arsenide has been dissolved within the gallium solution filling portion 10c of container 10. When additional gallium arsenide is no longer available to go into solution within portion 10c of container 10, gallium arsenide crystal growth onto seed crystal 19 can be terminated. If desired, however, gallium arsenide crystal growth can be stopped at any time by the operator by lifting seed crystal 19 together with resulting grown crystalline gallium arsenide thereon completely out of contact with the gallium solution within portion 10d of container 10.

It is thus seen that in accordance with the practices of this invention a simple, substantially trouble-free and convenient method of growing crystals is provided, no continuous drawing or pulling or vertical movement of seed crystal 19 together with the crystallized material (gallium arsenide) thereon being required, since, in effect, the resulting grown crystal (crystalline gallium arsenide) actually grows out of solution, the solution serving as a source of the crystalline material to be grown (gallium arsenide) and inherently drawing away from the resulting grown crystalline material (gallium arsenide).

Further exemplary of the practice of this invention, a suitable apparatus of the type illustrated in FIGS. 1 and 2 of the drawings may have the following dimensions; height of container,  $h$ , about 20 mm., diameter of container,  $d$ , about 30 mm., diameter of tube  $d'$ , about 15 mm., height of tube,  $h'$ , about 15 mm.

It is to be noted that in accordance with the practice of this invention, as clearly illustrated in the figures, heating element 11 surrounds the outside wall of container 10. Desirably, heating element 11 is not brought in heat exchange relationship with the bottom 10a of container 10, so that no substantial amount of heat transfer occurs between the heating element 11 and the gallium solution

within tube 12, particularly within portion 10d of container 10, without first passing through the gallium solution in portion 10c of container 10, thereby better maintaining and controlling the temperature gradient between the gallium solutions in portions 10c and 10d of container 10.

The crystal size and rate of crystal growth in accordance with the practices of this invention are to a certain extent controlled by the actual dimensions of the apparatus itself, larger and wider crystals tend to be grown with an increase in  $d''$  and longer, narrower crystals tend to be grown with a decrease in  $d''$ .

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many modifications, alterations and substitutions are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

Apparatus for growing a crystal from a solution containing crystal forming material dissolved in a solvent, comprising an outer container and an inner tubular container disposed in an upright position within said outer container, said inner tubular container being opened at both ends thereof with the lower of its ends being disposed within said outer container and spaced from the bottom of said outer container, a washer joining together said outer container and said inner tubular container and positioned higher than the lower end of said inner tubular container, said washer and the portions of said outer container and inner tubular container that extend below said washer together forming an outer chamber, said washer and said portion of said inner tubular container extending below said washer together forming a liquid impermeable barrier, so that said outer chamber communicates with the inner tubular container only at the bottom of the chamber, whereby the chamber and the inner tubular container may

contain a solvent which flows freely therebetween but a solid crystal forming material included within the solvent in said chamber and of a specific gravity less than the specific gravity of said solvent is contained within said chamber against said washer, a crystal holder for positioning a seed crystal in contact with the upper surface of said solvent in said inner tubular container, and a heating coil positioned outside of the outer container for heating the solvent in the outer container and inner tubular container, whereby the solvent in the chamber is maintained at a higher temperature than the solvent in the inner tubular container so that the solvent in the chamber is saturated with dissolved crystal forming material and the solvent in the inner tubular container is supersaturated with dissolved crystal forming material.

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