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CRYSTAL GROWTH TUBE

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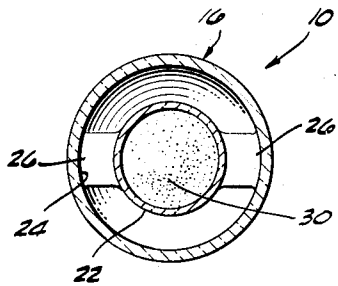


FIG. 2.

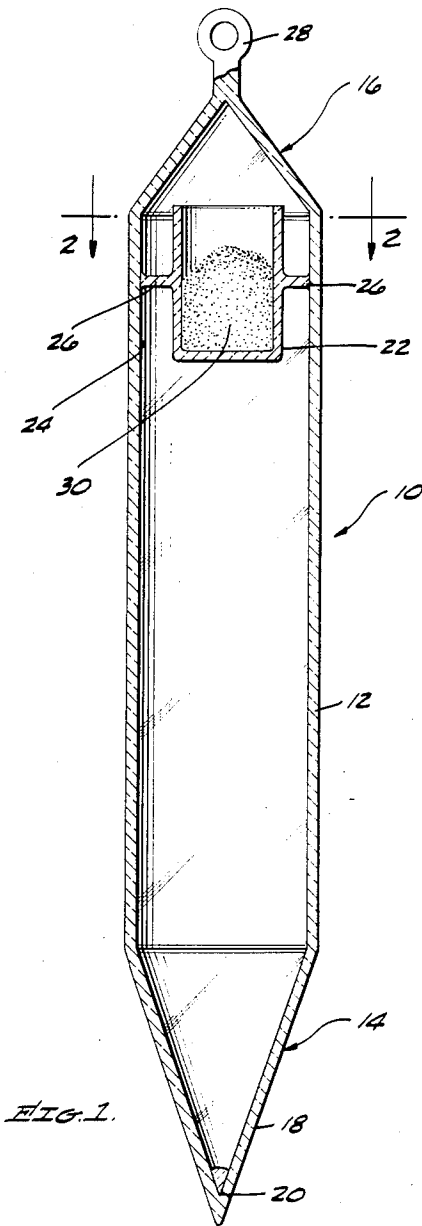


FIG. 1.

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CRYSTAL GROWTH TUBE

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Application May 22, 1967, Ser. No. 640,303, now Patent No. 3,519,399, dated July 7, 1970, which is a continuation of application Ser. No. 400,723, Oct. 1, 1964. Divided and this application Nov. 20, 1969, Ser. No. 878,498

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U.S. Cl. 23—273 R

10 Claims

ABSTRACT OF THE DISCLOSURE

A method of simultaneous purification and growth of semiconductor material into a single stoichiometrically pure crystal by sublimation and condensation of the material. The tube, which is useful for crystal growth for example by either a Bridgman process or by a vapor growth process, comprises a single body having a small container is secured in the upper tube part to contain the charge and a nucleation point in the lower tube part for growth of a single crystal.

This application is a division of copending application Ser. No. 640,303 filed May 22, 1967, now U.S. Pats. No. 3,519,399, patented July 7, 1970, which in turn is a continuation of application, Ser. No. 400,723, filed Oct. 1, 1964, now abandoned, both entitled "Method for Growing Single Crystals of Semiconductors."

The present invention relates to a crystal growth tube which is useful, for example, for simultaneous purification and growth of semiconductor material into a single crystal by sublimation and condensation of the material by means of either a modified Bridgman process or by means of a vapor growth process.

As a background for the present invention, the crystal growth tube was devised to overcome crystal growth problems associated with the Bridgman and vapor growth processes. In the Bridgman method, the charge is placed in a suitable crucible which is slowly lowered through a furnace having a temperature curve or profile, including a decreasing temperature gradient. The curve is provided with an initial portion which is above the melting point of the charge and a decreasing temperature or freezing gradient which passes through the melting point of the charge. Thus, the charge is first melted in the initial portion of the temperature profile and is subsequently solidified as the crucible and charge pass through the freezing gradient. The solidification progresses at a rate which corresponds to the speed of movement of the charge as it passes through the freezing gradient. Stoichiometrically pure cadmium telluride, for example, which is cadmium telluride free from excess cadmium or excess tellurium, can be obtained by the use of the Bridgman method if the charge material in the crucible is stoichiometrically pure. However, if the cadmium telluride or other semiconductor charge material initially placed in the crucible is not stoichiometrically pure, the crystals obtained by the use of the Bridgman method also generally are not stoichiometrically pure.

The present invention is adapted to overcome this and other problems by enabling the production of stoichiometrically pure crystals from stoichiometrically impure starting materials by either a modified Bridgman or a vapor method. Essentially, the charge material is physically segregated or separated from the growing crystal material. To achieve this result, a novel crystal growing tube is utilized. The tube comprises an upper portion having a cup secured thereto and a lower portion terminating in a nucleation point. Both the cup and the lower tube portion

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open into the tube in the same direction. The starting or charge material is placed in the cup and the tube is evacuated and sealed. The sealed tube is then placed within a furnace provided with a specified temperature curve or profile. Depending upon whether a modified Bridgman method or a vapor growth process is used, the initial portion of the temperature curve is above the melting point of the charge material or is immediately below the material's melting point. The initial portion is above the melting point when the modified Bridgman method is used and below the melting point when the vapor growth method is employed.

With either method, the charge material vaporizes in the initial portion of the temperature profile portion of the furnace. As the tube is lowered through the furnace and the temperature profile, the nucleation point passes through further portions of the curve. These further portions comprise a decreasing temperature gradient, are at temperatures which are lower than that of the initial portion, and contain a freezing gradient at which point the vaporized charge stoichiometrically combines and ultimately forms into a stoichiometrically pure crystal.

In the modified Bridgman method, the vaporized charge first condenses into a liquid which then solidifies as the tube passes through the freezing gradient. In the vapor growth method, the vaporized charge material directly condenses into a solid. The vapor growth method is advantageous when a low temperature growth of the crystal is desired.

The specific temperatures within the furnace are dependent upon the physical characteristics of the compound crystal and its ingredients. For example, the present invention has been adaptable to the formation of crystals selected from the Group II and Group VI elements of the Periodic Table, for example, combinations of zinc, cadmium and mercury with sulfur, selenium and tellurium.

The tube is further arranged so that the influence of gravity may be utilized. Many crystal materials do not adhere to the tube and, therefore, it is not possible to place the nucleation point at the upper portion of the tube.

By means of the present invention segregation of the starting charge from the crystal can be simply obtained by placing the charge material in the upper portion of the tube and the crystal growth portion in the lower portion of the tube to take advantage of the influence of gravity and to overcome any problems which may arise when the crystal does not adhere to the tube. In addition, the present invention also permits easy removal of the formed crystal from the tube because special procedures are not required to enhance adhesion of the crystal to the tube.

Therefore, the tube comprises an elongated cylinder having a nucleation point at one end and a cup or receptacle secured to the interior of the cylinder at the other end. Both the cup and the end have the nucleation point open in the same direction. The tube may be formed from any material which is nonreactive with the crystal materials and which can withstand the temperatures and pressures employed in the process. Quartz is preferred as the tube material; however, any material which conforms to the above conditions is suitable.

Accordingly, it is an object of the present invention to provide a novel crystal growth tube.

It is another object to provide a tube whereby stoichiometrically pure single crystals can be synthesized from starting materials that are not stoichiometrically pure.

Other aims and objects, as well as a more complete understanding of the present invention will appear from the following explanation of an exemplary embodiment and the accompanying drawings thereof, in which:

FIG. 1 is an elevational view, in longitudinal section, showing a crystallization tube comprising a cup for con-

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taining a charge material mounted in the upper part thereof and above the nucleation point in the lower part thereof and FIG. 2 is a cross-sectional view taken along line 2—2 of FIG. 1.

Accordingly, a tube 10 formed from quartz, for example, comprises an elongated body 12 having a lower portion 14 and an upper portion 16. A nucleation tip 18 terminating in a point is at the lower end. A quartz cup or receptacle 22 is positioned within the tube at its upper portion and affixed to the interior surface 24 by supports 26. A lowering rod may be secured to upper portion 18 by means of a loop 28.

Tube 10 is adapted to be placed within a furnace having a temperature curve or profile with an initial isothermal portion and lower temperature portions, including a decreasing temperature gradient. The initial portion has a length which at least equals the length of tube 10.

In operation, a charge 30 of starting material, such as cadmium telluride, is placed within cup 22. The tube is then evacuated and sealed.

Charged, evacuated and sealed tube 10 is lowered into the flat isothermal portion of the temperature profile of the furnace. In the modified Bridgman embodiment, the isothermal portion is above the melting point of the charge and is retained there for a time sufficient to permit the temperature to stabilize. The tube then is lowered through the furnace at a rate commensurate with the vaporization of the charge and formation of the crystal until the tube clears the furnace. During the movement through the furnace, charge 30 vaporizes from cup 22 and collects at tip or point 20 of tube 10 in a stoichiometrically pure form of a liquid or melt as tip 20 passes through the gradient. As the collected liquid in the tip further passes through the decreasing temperature gradient which contains the freezing point, a crystallite 32 nucleates at tip 20 and subsequently the crystallite grows as tube 10 is slowly moved further through the furnace and as additional vapors condense and crystallize.

In the vapor growth embodiment of the present invention, the maximum portion of the temperature profile of the furnace is maintained at a temperature which is below the melting point of the starting materials so that, as tube 10 and the charge is lowered through the furnace, the charge vaporizes and then solidifies into crystal 42 at tip 12 without passing through a liquid phase.

Although the invention has been described with reference to a particular embodiment thereof, it should be realized that various changes and modifications may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A single piece crystallization tube comprising an elongated integral body sealed about its entire periphery to exclude gas flow from a source external to said integral body, said body comprising a first portion and a second portion spaced from and sealingly affixed to said first portion, said first portion having a closed end and said second portion being open towards said closed end, a receptacle held within said first portion and separate from said second portion for receiving a charge of material, said receptacle having opening means facing said closed end, and said second portion providing a site for formation of a crystal from the charge of material.

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2. A single piece crystallization tube sealed and closed about its entire periphery to exclude gas flow from a source external thereto comprising a first portion having receptacle means wholly contained and retained within said first portion for receiving a crystal charge material and a second portion spaced from and integrally connected to said first portion for receiving vapors from the crystal charge material and for nucleating crystals from the vapors.

3. A tube as in claim 2 wherein said receptacle means includes opening means and said second portion includes opening means, said opening means of said receptacle means and said second portion both opening in the same direction.

4. A tube as in claim 2 wherein said receptacle means has closure means and said second portion has closure means, said closure means of said receptacle means and said second portion facing in the same direction, and said first portion placeable above said second portion to permit gravity to separately maintain the crystal charge material in said receptacle means and the crystal in said second position.

5. A tube as in claim 2 wherein said first portion receptacle means comprises a receptacle integrally affixed to said first portion for receiving the charge material.

6. A tube as in claim 5 including support means integrally affixing said receptacle to said first portion.

7. A tube as in claim 6 wherein said support means comprises at least one extension secured to said first portion and to said receptacle.

8. A crystallization tube for growth of crystals in a vertical crystal growth furnace comprising an integral, one-piece, elongated body sealed about its entire periphery to exclude gas flow from a source external to said integral body and having an upper portion and a lower portion, said lower portion having a nucleation tip for the growth of the crystals, and a receptacle affixed to said upper portion for receiving and containing solid and liquid charge materials to be vaporized into nucleation of the crystals at said nucleation tip.

9. A tube as in claim 8 further including support means secured to the inner surface of said body and to said receptacle for affixing said receptacle to said upper portion.

10. A tube as in claim 8 wherein said receptacle comprises a cup having an outer periphery of dimension less than the dimension of the inner periphery of said upper portion.

References Cited

UNITED STATES PATENTS

2,836,524	5/1958	Brenner et al.	23—273
2,944,878	7/1960	Jacque et al.	23—294
3,014,791	12/1961	Benzing et al.	23—294
3,031,261	4/1962	Vogel et al.	23—294
3,093,517	6/1963	Lyons	23—294
3,260,573	7/1966	Ziegler	23—273
3,338,761	8/1967	Cheney et al.	23—273

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