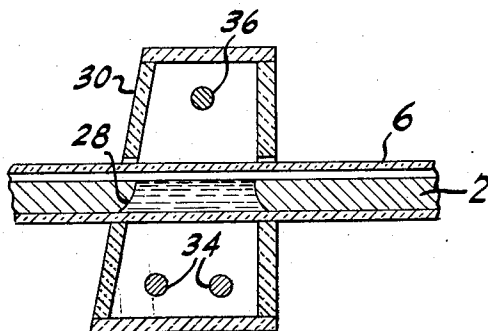
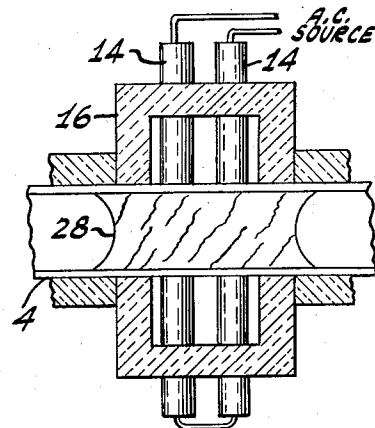
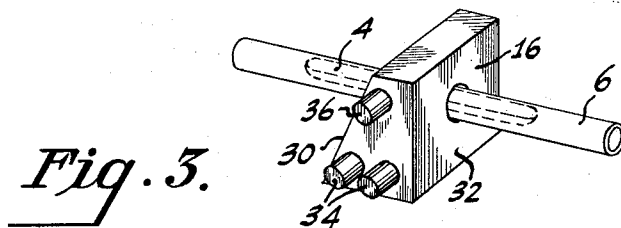
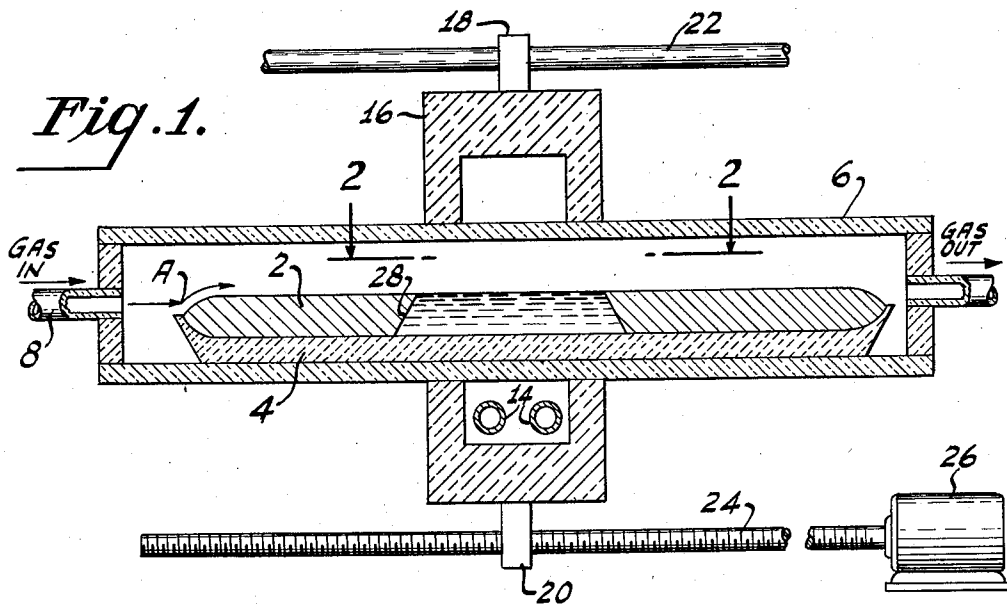


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METHOD FOR SINGLE CRYSTAL GROWTH

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METHOD FOR SINGLE CRYSTAL GROWTH

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This invention relates to improved methods for growing single crystals by zone-melting and more particularly to growing such crystals without the necessity of an initial seed crystal.

Heretofore, in the preparation of semi-conductor materials, for example, it has been customary to grow a single crystal of a substance by melting the substance and contacting a seed crystal of the substance to the melt and then either slowly withdrawing the seed or slowly moving the melting zone of heat along the material and away from the seed. In either case the molten substance freezes-out on the seed crystal and grows as a single crystal therefrom along an axis determined by the orientation of the seed crystal. In the moving zone-melting system just described, it is, of course, possible to keep the heating zone stationary while moving the material to be melted and re-crystallized.

There are many reasons why it is desirable to grow single crystals without requiring a seed crystal. The seed crystal is a valuable crystal which could be used, in the case of germanium and silicon, to make a large number of semi-conductor devices. This is especially true since the seed crystal must be large enough to be securely gripped by a chuck or other supporting apparatus. The use of a seed crystal to grow additional crystals therefore represents waste.

Difficulty has been encountered in the past in growing single crystals because of the formation of small nucleating centers in the growing crystal resulting in the growth of disoriented crystals. This is true whether the crystal is being grown from a seed crystal or not. Sources of such undesired nucleating centers are discontinuities in the container walls. Such crystals tend to grow in a direction normal to the walls of the container. If the advancing interface between the liquid and solid phases of the material is at right angles also to the walls of the container and hence parallel to or coincident with the direction of growth of crystals from these nucleating centers, the extent of their growth into the principal crystal is considerable.

It is therefore an object of this invention to obviate the necessity for a seed crystal in growing a single crystal of a substance by the zone-melting technique.

Another object is to reduce the formation and development of multiple nucleating centers in the process of growing single crystals.

A further object of the invention is to control the shape of the interface between the solid and liquid phases of a growing single crystal so as to minimize the effect of accidental nucleation of secondary crystals with respect to the growing of a single crystal.

Another object of the invention is to establish an interface inclined with respect to the vertical between the solid and liquid phases of a growing single crystal in a zone-melting furnace while maintaining the horizontal shape of the interface convex.

An additional object is to grow without seed a single crystal of a substance in a zone-melting furnace while

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maintaining the shape of the interface between the liquid-solid phases of the growing single crystal as horizontally convex and vertically inclined.

Another object is to provide improved methods of growing ingots of single crystal material.

These and other objects and advantages of the invention are accomplished, for example, by so heating an ingot of the substance to be melted and re-grown as a single crystal as to establish a vertical temperature gradient from the top to the bottom of the substance. This establishes, in turn, an inclined interface between the liquid-solid phases of the ingot with the length of the molten phase being greater at the bottom than at the top of the ingot. By exposing the sides of the ingot to a heat source for a longer period than the bottom thereof, the sides remain molten longer. Thus the center of the melt freezes-out first and the sides last, to establish a horizontally convex shape of the solidifying interface. Thus by establishing the liquid-solid interface at an angle with respect to both the bottom and side walls of the container, crystals originating from undesired nucleating centers thereat meet and stop growing at the advancing boundary of the principal crystal while still relatively small. Finally, by reducing the temperature of a small area of the melt to about the freezing point thereof desired small area nucleation takes place thereat and single crystal growth is initiated therefrom.

The invention will be described in greater detail with reference to the drawings in which:

Figure 1 is a partially schematic cross-sectional side view of a horizontal zone-melting furnace used according to the method of this invention,

Figure 2 is a partial cross-sectional plan view of the furnace of Figure 1 taken along the line 2—2' thereof,

Figure 3 is a perspective view of another embodiment used in the method of applicants' invention, and

Figure 4 is a partial view in section of the embodiment shown in Figure 3.

Like numerals represent similar elements throughout the drawings.

A single crystal of a substance such as germanium or silicon for example may be grown without a seed crystal utilizing the apparatus shown in the drawings. An ingot 2 of germanium is placed within an elongated carbon boat 4. The side walls of the boat 4 should be low enough to expose as much of the ingot 2 as possible while serving to support the ingot in its molten phase. Inasmuch as only a small portion of the ingot 2 is molten at a given time surface tension will permit a relatively large vertical exposure of the molten phase without side-wall support. As will be explained later this is an important feature of the invention.

The elongated boat or crucible 4 is placed within a refractory tube 6 that may be of quartz and is provided with inert gas inlet and outlet means 8 and 10. The tube 6 and the crucible assembly are surrounded by a zone-melting furnace 16 which extends longitudinally along a relatively small portion of the length of the assembly.

The zone-melting furnace 16 may be heated by any convenient means such as the electric resistance heating elements 14 connected to any convenient power source, not shown. The furnace 16 is adapted to travel along the length of the boat 4 from one end to the other at a controlled rate. Any convenient means may be provided to propel the furnace 16 along the tube 6. For example, the furnace 16 may be supported by the two brackets 18 and 20. The bracket 18 is suspended from the rail 22 while the bracket 20 rests on the screw 24. The screw 24 may be rotated by the motor 26 to propel the furnace in a desired direction at a controlled speed. Alternatively, the furnace 16 may be held stationary

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and the crucible 4 may be adapted to progress through the furnace.

In typical apparatus the elongated vessel 4 may be about 24" long and 1" in width, for example, and the germanium ingot 2 may weight about 1 kilogram. In operation, a protective gas such as hydrogen or an inert gas is maintained within the tube 6.

In operation the motor 26 is started and the furnace 16 is driven slowly along the length of the tube 6 and the crucible 4. The electrical resistance heating elements are supplied with power so as to raise the temperature within the furnace to at least 50° C. above the melting point of the material of the ingot 2, which in the case of germanium is about 900° C. Thus as the crucible 4 and the ingot 2 enter the furnace the ingot 2 becomes molten. The temperature of the molten zone is not critical except that it should be substantially higher than the melting point of the ingot 2 so as to insure complete melting of the entire mass of the ingot within the furnace 16. Furthermore, if the temperature of the molten zone is kept at a point only slightly above the melting point of the ingot 2, relatively small solid crystallites of the material may remain in the molten zone without melting. These crystallites may provide additional nucleating centers as the zone progresses and interfere with the growth of a large single crystal.

As the furnace 16 is driven along the length of the crucible 4, a continually changing portion of the ingot 2 is melted and re-frozen. Due to the fact that the heat source (electric resistance elements 14) is located beneath the crucible 4 and the ingot 2 the bottom portions of the ingot 2 melt first and freeze-out last. The top portions of the ingot 2 melt last and freeze-out first. This means therefore that the interface between the molten-solid phases of the ingot 2 is at an inclination with respect to the perpendicular to the floor of the crucible 4. As pointed out previously, small nucleating centers originating at discontinuities of the crucible wall will tend to grow crystals in a direction normal to the crucible walls. By having the interface between the molten-solid phases reach such nucleating centers as soon as possible this undesired crystal growth can be checked while the crystals are relatively small. This is accomplished by the inclined interface between the molten-solid phases of the ingot 2 as provided by the invention as far as the floor of the crucible 4 is concerned.

One way to instigate nucleation of a crystal in a molten mass is to cool a small area of the mass to the point of solidification and then to continue freezing-out successive portions of the molten mass adjacent to the small nucleating area. The invention takes advantage of this technique and also of the inclined interface between the molten-solid phases of the ingot 2 to grow a large single crystal without the necessity of a seed. To do this a stream of inert gas is directed against the forward molten surface of the ingot 2 so as to strike the ingot surface at the point A. The flowing inert gas reduces the temperature of the melt at point A to about the freezing point of the ingot 2 whereupon a small nucleating center is formed. As the furnace 16 continues to pass over the tube 6 and the crucible 4, the slanted interface 28 moves along likewise resulting in the freezing-out of the top portions of the melt first. Thus the nucleating center is formed by the cooling gas stream at point A and then the portions of the melt immediately adjacent thereto are successively frozen-out by the movement of the melting zone to grow a single large crystal from the nucleating center.

The ingot 2 is also in contact with the side walls of the crucible 4. Therefore any discontinuities in these walls will also tend to form nucleating centers and hence undesirable crystal growth. To inhibit such crystal growth the invention causes the interface between the liquid-solid phases to be horizontally convex. Referring to Figure 2 the interface 28 is shown as being convex

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with the outermost portions of the ingot 2 freezing-out after the center of the ingot has solidified. Since crystal growth tends to progress in a direction normal to the interface, a convex shaped interface, therefore, provides a freezing-out front such that undesired non-uniform crystal growth tends to extend toward the outer edges of the ingot and not to continue along the length of the ingot. The convex shape of the ingot 2 is achieved according to the invention by causing the sides of the ingot to receive more heat than the center portions. As shown in Figure 2, the side portions of the ingot 2 which are exposed above the crucible walls, are exposed to direct radiation from relatively long lengths of the heating elements 14 during the passage of the ingot 2 through the furnace 16. This means also that these side portions of the charge adjacent the entrance and exit of the heating chamber of the furnace are raised to a higher temperature than other portions of the charge 2 which are relatively protected from the heat by crucible 4. Hence the side portions of the ingot 2 are maintained molten longer than the center portions thereof resulting in the desired convex interface between the liquid-solid phases of the ingot.

The rate of travel of the furnace to most advantageously achieve maximum crystal growth is only slightly variable. Several factors must be considered such as the rate of maximum crystal growth, the kind of material involved, and the temperature of the melt. In growing a single crystal of germanium, for example, a speed of about 1 to 3 mm. per minute gives satisfactory results when the molten zone is maintained at about 50° C. above the melting point of germanium.

When the furnace 16 has traversed the entire length of the crucible 4, the entire ingot 2 has been converted to a single crystal and the process is complete.

The method of heating the zone furnace 16 is not critical. Electric resistance elements such as bars of silicon carbide known commercially as "Globars" are suitable.

In zone-melting metals such as germanium and silicon it is desirable to provide a protective atmosphere such as hydrogen or an inert gas to prevent oxidation of the heated metal and to minimize the introduction of impurities into the metal. The presence of a special atmosphere is desirable in many zone-melting applications; however, the provision of a protective atmosphere is not an essential part of the invention and may be omitted in certain instances such as when zone-melting chemically stable salts or oxides. In such cases a stream of air may be directed against the forward surface of the molten ingot 2 in order to establish the nucleus for single crystal growth.

Figures 3 and 4 illustrating an alternative embodiment of the invention wherein the inclining interface 28 between the molten-solid phases of the ingot 2 may be achieved. In this embodiment the wall 30 of the furnace has an aperture which may serve either for the entrance or exit of the tube 6 and the vessel 4 containing the ingot 2. The wall 32 which is opposite the wall 30 likewise contains an aperture for the same purposes. The wall 30 is slanted toward the opposite wall 32 so as to provide a vertically tapering furnace chamber. The uppermost portion of the furnace 16 is thus smaller in length between the walls 30 and 32 which contain the exit and entrance apertures. If desired, of course, both walls 30 and 32 could be sloped toward each other to obtain the same internal furnace chamber shape. Two electric resistance heating elements 34 are provided in the bottom of the furnace 16 while one element 36 is located in the narrowed top portion. This permits not only more rapid melting of the ingot but also provides a better control of the vertical temperature gradient inside the furnace 16. The arrangement of the heating elements also provides additional underside heating of the ingot 2. As the ingot 2 moves through the furnace 16 the top portion receives less heat than the bottom portion. This is be-

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cause of the arrangement of the heating elements and because of the shortness of the travel path in the upper part of the furnace in comparison with the longer length of travel at the bottom part of the furnace. This means that the top portions of the ingot 2 melt last and freeze-out first in comparison with the bottom portions. This in turn provides the desired slanted interface between the liquid-solid phases of the ingot. It is evident, of course, that nucleation could be initiated at the interface by directing a stream of inert gas thereagainst. Likewise the horizontal shape of the interface can be rendered convex by the same technique as described in connection with the furnace of Figure 1. It will be noticed that the furnace shown in Figure 3 provides an extremely sharp gradient. Such a gradient is not only essential for single crystal growth but for homogeneity as well.

The practice of the invention is not limited to the particular materials described heretofore. It is equally applicable to zone-melting of other materials, such as metals generally and salts. Neither is the practice of the invention limited to any particular type of zone furnace. Any known means of providing a relatively narrow appropriately shaped moving zone of relatively high heat may be utilized.

What is claimed is:

1. In a method of growing a single crystal by horizontally zone-melting a horizontally disposed elongated body of material, the steps of: melting an end portion of said elongated body by applying more heat to the bottom than to the top thereof to establish a vertical temperature gradient therein whereby the uppermost parts of said portion of said elongated body become molten last and solidify first upon temperature decrease, the interface between the molten and solidified portions being thereby inclined, reducing the temperature of a predetermined area of an upper portion of said molten portion to about the freezing point thereof to establish an area of nucleation, and melting and freezing-out successive portions of said elongated body commencing with those portions adjacent to said predetermined area whereby a single crystal of said material is grown from said area of nucleation.

2. The invention according to claim 1 wherein said

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area of said molten portion is reduced to the freezing point thereof by directing a stream of inert gas thereagainst.

3. The invention according to claim 2 whereby successive molten portions of said elongated body are frozen-out by providing horizontal relative motion between said molten portions and the source of said heat.

4. In a method of growing a single crystal by horizontally zone-melting a horizontally disposed elongated body of material, the steps of: melting a portion of said elongated body, establishing a vertical temperature gradient in said elongated body decreasing toward the top thereof such that the top of said molten portion is at a lower temperature than the bottom thereof, establishing a horizontal temperature gradient in said elongated body increasing outwardly radially from the center thereof such that the side portions of said molten portion are at a higher temperature than the center portion thereof, whereby the interface between said molten portion and the adjacent solid portions of said elongated body is vertically inclined and horizontally convex, reducing the temperature of a small predetermined area of an upper portion of said molten portion to about the freezing point thereof for initiating single crystal growth at said interface, and melting and freezing-out successive portions of said elongated body whereby a single crystal of said material is grown.

References Cited in the file of this patent

UNITED STATES PATENTS

1,450,464	Thomson	Apr. 3, 1923
1,738,307	McKeehan	Dec. 3, 1929
2,615,060	Marinace et al.	Oct. 21, 1952
2,679,080	Olsen	May 25, 1954
2,789,039	Jensen	Apr. 16, 1957

OTHER REFERENCES

Schumacher: "Ultra Pure Metals Produced by Zone-Melting Technique," in "Journal of Metals," November 1953, pp. 1428-29.

Pfann: "Journal of Metals," vol. 4, July 1952, page 747-753.