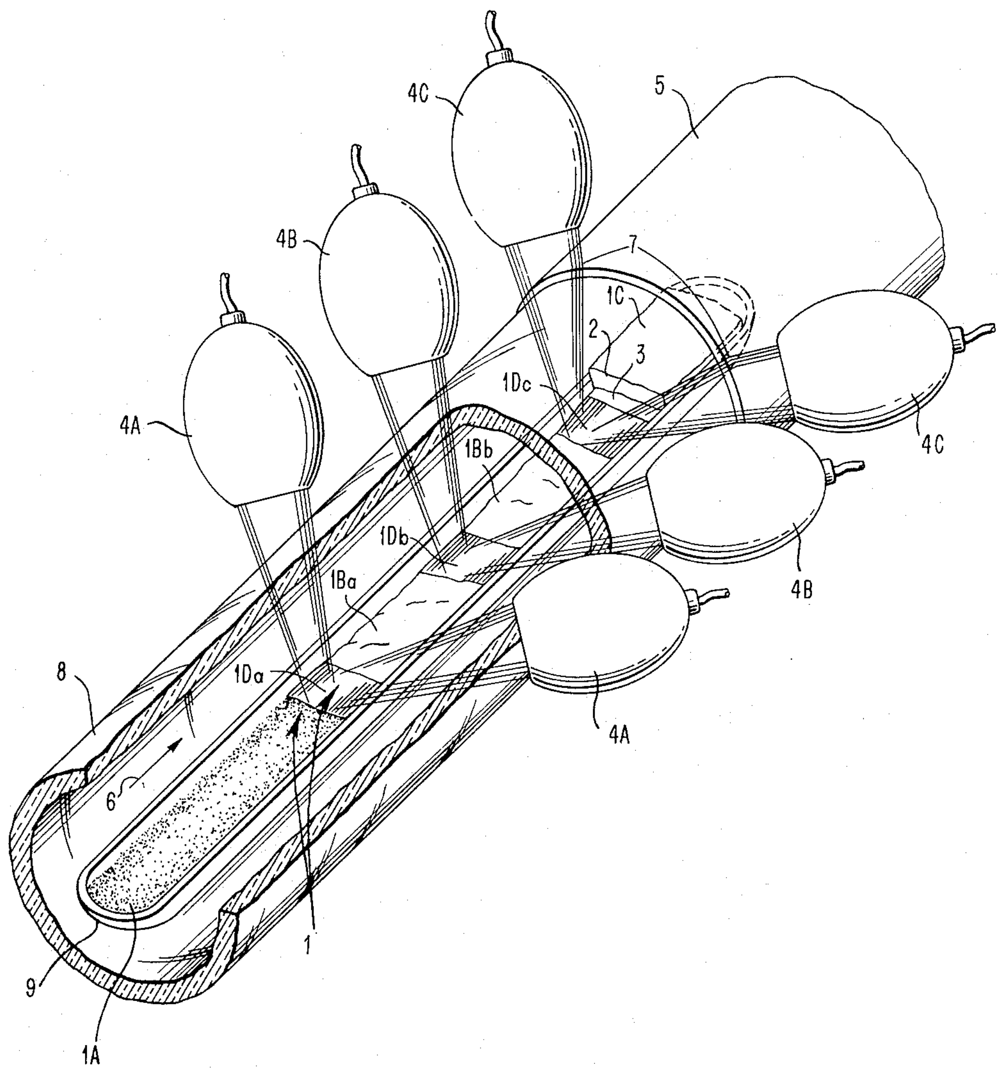
Feb. 6, 1962

G. R. GUNTHER-MOHR

3,020,132

SINGLE CRYSTAL REFINING

Filed April 30, 1959



INVENTOR
GERARD R. GUNTHER-MOHR

BY Alvin J. Riddles
ATTORNEY

United States Patent Office 3,020,132
Patented Feb. 6, 1962

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SINGLE CRYSTAL REFINING

Gerard R. Gunther-Mohr, Wappingers Falls, N.Y., assignor to International Business Machines Corporation, New York, N.Y., a corporation of New York

Filed Apr. 30, 1959, Ser. No. 809,957
9 Claims. (Cl. 23—301)

This invention relates to the purification of materials and in particular to the process of single crystal zone refining of material.

In many applications it is advantageous to provide a material of extremely high controlled purity in the form of a single crystal.

The semiconductor material used in such devices as transistors is in the form of a single crystal in which a very high degree of purity is maintained and into which a very closely controlled quantity of deliberately introduced impurities have been added. The order of magnitude of the relationship of impurity atoms to semiconductor atoms in the single crystal is frequently as great as one impurity atom to ten million crystal atoms. In order to provide the desired single crystalline purity, techniques beyond the standard chemical purification techniques have been employed. A most widely used one of these techniques involves the principle that an impurity has a greater affinity for the molten state than the solid state so that a molten region may be employed to sweep out of a quantity of a material all impurities present therein so that a very closely controlled quantity of the proper type of impurities may be added at a later step. The high purity refining technique has been developed considerably in connection with the semiconductor art. As the art has thus far developed, there have been two variations of this technique employed to provide semiconductor material useful in transistor and other semiconductor device manufacturing. These variations have been known as "zone refining" where the molten region is employed to purify the material, and, "zone leveling" where the molten region is employed to evenly distribute a given quantity of a particular impurity throughout a quantity of semiconductor material.

The technique of "zone refiining" has been described in the publication "The Transactions of the American Institute of Metallurgical Engineers," vol. 194, page 141, 1952, by W. G. Pfann.

The technique of "zone leveling" is described in the "Bell System Technical Journal," vol. 35, page 637, 1956, by D. C. Bennett and B. Sawyer.

Efforts have been made in the art toward the growing of a single crystal of semiconductor material in connection with a zone leveling operation by providing a seed crystal along with the semiconductor material. These efforts have been reduced in effectiveness by a problem arising from the fact that the heat involved in the operation, operating on the seed, melts portions of the seed which may contaminate the melt, and no provision has been made in the past to control the amount of such melting in such operations.

What has been discovered is a technique whereby a zone refining and/or leveling operation may be combined with a proper arrangement of conditions of heat application and seed shielding structure to result in the growth of a single crystal of material between all molten zone passes in a single operation which operates to control the variation of the segregation coefficient due to segregation at grain boundaries and thereby to attain a higher degree of crystal purity than has heretofore been available in the art.

It is an object of this invention to provide a technique for growing a pure single crystal from an unrefined quantity of semiconductor material in a single operation.

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It is an object of this invention to provide a technique for growing a pure single semiconductor crystal from an unrefined quantity of semiconductor material in a single operation.

It is another object of this invention to provide a control of the heat applied to a seed crystal during a crystal growing operation.

It is another object of this invention to permit a seed crystal to pass through a heated region in a single crystal zone refining operation.

It is another object of this invention to control the amount of melting of a seed crystal during a zone refining operation.

It is another object of this invention to enable the growth of single crystals during a zone refining operation.

It is still another object of this invention to provide a control of the heat present at a freezing interface in a radiant heating molten region refining operation.

It is still another object of this invention to provide a control of the heat present at a freezing interface in a radiant heating molten region semiconductor refining operation.

Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawing which discloses by way of example the principle of the invention and the best mode which has been contemplated of applying that principle.

In the drawing:

The figure is a schematic illustration of the structural conditions present in the single crystal zone refining technique of this invention.

Referring to the figure, there is shown a container with a charge of a material capable of being zone refined and capable of absorbing infra-red energy. Among such a class of materials are organic compounds such as anthracene and many dielectrics. For purposes of illustration, semiconductor material undergoing a single crystal refining operation in accordance with the invention, has been selected. The semiconductor material is labeled element **1** and is illustrated in an intermediate stage of refining wherein the material **1** is shown as having an unrefined portion **1A**, two partially refined single crystal portions **1B**, and a refined portion **1C**. Each of these portions is separated from its adjacent portion by a molten zone **1D**. The semiconductor material may be any material in which the impurities have a greater affinity for the liquid state than the solid state and which have a monocrystalline form, the monoatomic semiconductors such as germanium and a silicon and the intermetallic compounds such as indium antimonide are examples. As illustrated, section **1A** is shown as being an amorphous group of particles and, of unrefined semiconductor material, when a first molten zone passes, it is transformed into a single crystal section **1B***a* and wherein molten zone **1D***a* contains a large quantity of impurities present. The second molten zone labelled **1D***b* in passing, further refines the semiconductor material. The third illustrated molten zone labelled **1D***c* still further refines the semiconductor material and as each molten zone progresses serially away from the seed crystal, the molten semiconductor material solidifies in an epitaxial manner on the seed crystal 1C, and, as each molten zone progresses along the length of the material **1**, a single crystal of refined semiconductor material will grow in the direction of travel of the molten region from the seed crystal 1C. In the drawing the seed crystal 1C is illustrated as being somewhat larger in cross-sectional area than the semiconductor material to show a line of demarcation although it will be apparent that no size requirement of the seed is essential and the said crystal **1C** terminates at a face **2** so that, as illustrated, a single crystalline semiconductor material labelled **1B***a*, **1B***b* and **3** has grown from the original seed crystal face **2**. Sufficient heat is applied to the semiconductor material **1**, in regions where molten zones are desired by a heat source which for example, may be by way of elliptical radiant heater reflectors **4**, arranged in sufficient plurality for the number of molten zone processes desired. It has been found advantageous for uniform heat transmission to provide the reflectors in pairs. In the case of the pair of reflectors 4A, these sources provide sufficient heat for the first molten zone 1D*a*. The pair of radiant heaters 4B provide sufficient heat for the second molten zone 1D*b* and the pair of radiant heaters 4C provide sufficient heat for the third illustrated molten zone 1D*c*.

It has been determined and reported in the above described literature that the effectiveness of a single pass of a molten zone in a zone refining process depends on the segregation coefficient, which is a ratio of the concentration of impurities in the solid to the concentration of impurities in the liquid, and, on the ratio of the zone size to the bar length. A serious problem has been encountered in the art in that the segregation coefficient is substantially influenced by grain boundaries in the material which cause preferential segregation and thus interfere with the purity of the refined crystal. It has been further found that the melting of portions of the seed crystal containing impurities operates to introduce contamination to the molten region and hence to reduce the effectiveness of the refining operation.

Through the technique of this invention a heat control is provided for the seed enabling the seed to pass through the heating zones and to permit formation of a single crystal between each molten zone thereby keeping the segregation coefficient from being influenced by grain boundary formation and reducing the amount of the seed that is melted to contaminate the refined material.

It has been found that through the use of a heat control associated with a seed crystal and a freezing interface, single crystals may be grown in a molten zone refining operation wherein the seed crystal actually passes through the regions being heated and at the same time, crystals are achieved that have a greater purity.

In accordance with the invention, a heat control **5**, is provided to control the temperature of the seed crystal **1C**, the freezing interface, and to prevent the heat from the radiant heaters **4** applying the heat to the seed crystal when it passes under the heaters. The sources of heat **4**, may be in addition to the radiant heaters illustrated, any sufficiently intense and controllable source of heat capable of producing a defined molten region in the semiconductor material. It has been found that the heat controlling element **5** may be any structural arrangement that is capable of exercising in the region of the seed and the freezing interface, a control on the amount of heat transferred from the heating source to the semiconductor material. The element **5** serves a dual purpose in that it prevents direct heat application to the seed 1C where it is drawn through a heated region and it controls heat dissipation in the vicinity of the freezing interface by reducing the temperature gradient thereby providing better quality crystals.

The dimension of the width of the molten zone in practice, is found to be quite critical in that it determines the number of molten zones that can traverse a given quantity of semiconductor material in a single pass, and the maximum purity achievable. The molten zone width must be approximately equal to the bar thickness in order to insure that all the material is melted in each pass of a molten zone. It is found that the radiant heaters are quite convenient in that they can be focused to provide a very narrow molten region. In order to establish proper perspective, the molten zone length in practice, is of the order of 0.2 inch, and, in the case of the technique known in the art as floating zone refining, the molten zones **1D** are sufficiently narrow that surface tension of the molten material tends to hold it in position. The shield **5** may be of any suitable material which will provide a sufficient reduction in temperature in the area of the seed crystal 1C that it will not melt when passed under the heaters **4** and that will reduce the temperature gradient between solid and liquid. In this illustration, involving radiant heaters, aluminum foil has been found to be quite satisfacotry. Relative motion with respect to the sources of heat **4** and the semiconductor material **1** is indicated by the arrow **6**. The relative motion may be in any constant direction so long as the successive molten zones 1D*a–c*, separated by single crystal zones 1B*a* and 1B*b* progress serially away from the region in which the seed crystal 1C is located. Where the seed 1C is drawn through the heating zones the heat control element **5** travels with it and shields the seed from the heat as by breaking up the heat transfer as shown by the break in the radiant rays at points **7**.

In order to maintain the degree of purity required of semiconductor material, molten region refining operations are carried out in an environment that is free of contaminating impurities and elements that are likely to enter into a chemical reaction with the semiconductor material. In practice, the refining operation is usually done in a sealed container, such as for example, a quartz tube labelled element **8**. The tube may be evacuated or a neutral gas is either sealed in the tube or is passed over the material **1** as during the refining operation. Under the conditions as described in connection with the figure, relative motion indicated by the arrow **6**, then will progress with the unrefined germanium material **1A** being first traversed by the first molten zone **1D*a*** so that a major portion of the impurities contained therein will be retained in the molten zone. The refined region 1B*a* is permitted to solidify after the zone **1D*a*** moves in the direction opposite to the arrow **6**. The second molten zone **1D*b*** passes progressively along the semiconductor material permitting the material to solidify in a more refined state. Similarly, the molten region **1D*c*** passes progressively along and the single crystal **3** grows from the face **2** of the seed crystal.

In order to establish a proper perspective and to provide a starting place for one skilled in the art in practicing the technique of this invention, the following set of specifications of molten zone refining single crystal growth operation in accordance with the invention are provided, it being understood that no limitation should be construed hereby since the provision of these specifications is made merely as a guide and it will be readily apparent to one skilled in the art that a wide variety of such specifications may be employed within the spirit of the invention.

Container **8** may be a quartz tube having sufficient structural ability to withstand a vacuum within the tube of 10^{-8} millimeters of mercury. The boat **9** may be of graphite approximately 12 inches long having a depression therein essentially 1 inch in diameter for the charge of semiconductor material. The seed crystal **1C** may be of monocrystalline germanium and at the face **2** is approximately 1 inch diameter, 2 inches long. The shield **5** may be 2 layers of aluminum foil approximately 0.010 inch thick and 5 inches long wrapped around the outside of the tube **7** if the heat sources **4** are stationary and the boat **9** is moved. In the event that the heat sources **4** are moved, the shield **5** may be a metal sleeve movable with the heat sources.

The radiant heaters **4** may be ellipsoidal reflectors having a 4 inch radius equipped with a one thousand watt bulb positioned at approximately the focus, located about 10 inches from the semiconductor material **1**. The rate of relative motion may be approximately 0.001 inch per second. The approximate width of the molten zone is 0.3 inch. The approximate distance between molten zones is 0.8 inch.

What has been described is a technique of passing a plurality of molten zones along a quantity of material simultaneously with presenting to the last zone a temperature controlled seed crystal and freezing interface capable of passing through the heated zones so that in a single refining operation, a single crystal is produced between molten zones resulting in a control of segregation coefficient and producing a single crystal having greater crystalline purity than heretofore available in the art.

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to a preferred embodiment, it will be understood that the various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art, without departing from the spirit of the invention.

It is the intention therefore, to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. A single crystal zone refining device comprising a longitudinally disposed quantity of zone refinable material, a plurality of sources of heat each capable of rendering a discrete portion of said material in a molten condition, each of said sources of heat being longitudinally disposed with respect to the other of said sources of heat so that each molten region in said material associated with a particular source of heat is longitudinally separated from the next adjacent molten region by a region of solidified single crystal material, means for providing relative motion parallel with a longitudinal direction of said material between said sources of heat and said material, a seed of monocrystalline material in contact with the portion of said material first traversed by a molten region and a heat controlling member operable to restrict the application of heat to said seed crystal.

2. The device of claim 1 wherein said material is semiconductor material.

3. The device of claim 2 wherein said semiconductor material is germanium.

4. In a single crystal zone refining operation an elongated body of semiconductor material, means applying heat only to a restricted narrow portion of said body, means for imparting relative motion between the source of said heat and said body, operable to cause a restricted narrow molten zone in said body to traverse the longitudinal axis of said body, a seed crystal in contact with the forward portion of said body in the direction of said relative motion, and shielding means controlling the amount of said heat applied to said seed crystal.

5. A single crystal zone refining apparatus comprising a controlled environment container, means maintaining

an environment within said container compatible with the growth of monocrystalline material, a quantity of material longitudinally disposed within said container, a plurality of radiant heating sources each focused to provide a small discrete molten zone in said material at specific spacings along the longitudinal dimension thereof separated by single crystal solidified semiconductor material, means providing relative motion in the longitudinal direction between said material and the focal points of said radiant heaters, a seed crystal in contact with said material and the focal points of said radiant heaters, a seed crystal in contact with said material in the forward most portion of said longitudinal dimension in the direction of said relative motion and shield means operable to control heat applied to said seed crystal.

6. The single crystal zone refining apparatus of claim 5 wherein said material is semiconductor material.

7. The single crystal zone refining apparatus of claim 6 wherein said material is germanium.

8. A method of single crystal refining comprising the steps of providing a seed crystal in contact with a quantity of longitudinally disposed material, providing a plurality of sources of heat each capable of rendering a discrete portion of said material in a molten condition, providing relative motion between said sources of heat and said material in a direction away from said seed crystal and providing shielding means controlling the application of heat from said source to said seed crystal.

9. A method of single crystal zone refining comprising, providing a longitudinally disposed quantity of zone refinable material in an environment compatible with the growth of single crystal monocrystalline material, providing a seed crystal in contact with one extreme of said longitudinally disposed material, providing a plurality of radiant heaters each focused on a discrete portion of said material rendering said discrete portion molten, providing motion to said molten region in a direction away from said seed crystal and providing shielding means controlling the application of heat to said seed crystal.

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