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METHOD AND APPARATUS FOR GROWING SINGLE  
CRYSTALS FROM MOLTEN BODIES  
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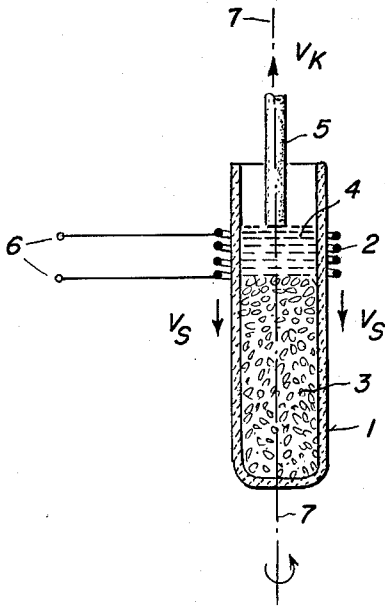


FIG. 1

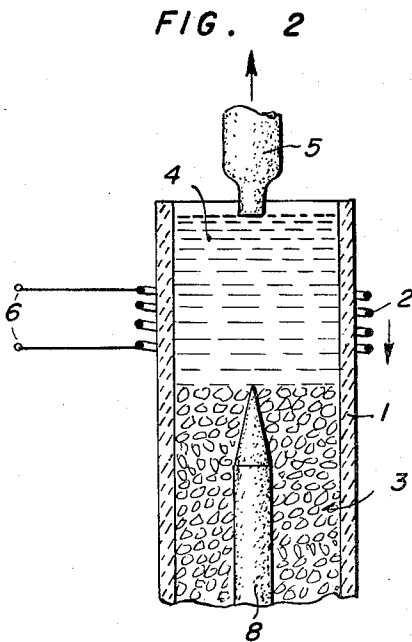


FIG. 2

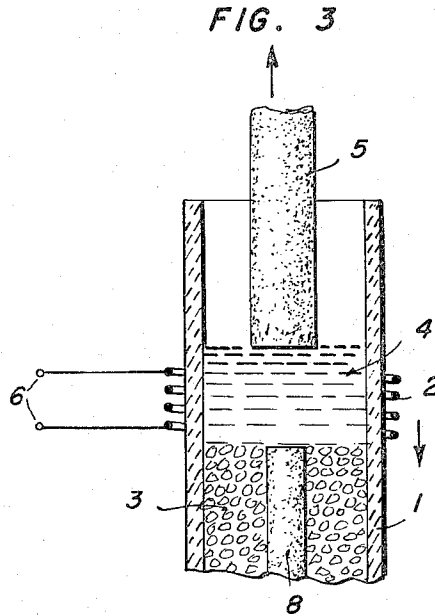


FIG. 3

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## METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS FROM MOLTEN BODIES

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The present invention relates to a method for growing single crystals from molten bodies and, particularly, from molten bodies of semi-conductors.

Methods of growing single crystals of various substances have previously been known. One method of growing a single crystal comprises melting a body of a substance and slowly withdrawing the single crystal from the melt with the aid of a seed crystal. Another method is the so-called zone-melting system, wherein a bar shaped body of a substance is associated at one end with a seed crystal and is caused to melt in a cross-sectional zone in the region adjacent to the seed crystal. This relatively narrow molten zone, which extends through the entire cross-section of the bar, is then allowed to travel in the longitudinal direction of the bar. This technique is usually carried out by placing the bar in a carbon or quartz crucible which is dimensioned to conform to the shape of the bar.

Although this method has the advantage over the first aforementioned method of yielding single crystals which have a substantially constant diameter and wherein the regions of impurity content are relatively evenly distributed, it has not been satisfactory because the surfaces of the crucible are apt to exercise a detrimental effect upon the growth of the crystals and the lattice structure of such crystals.

The object of the present invention is to provide a method that overcomes these disadvantages and makes possible the production of single crystals which have throughout their length, or at least throughout the major portion thereof, a homogeneous gradient-free distribution of the regions of impurities and which possess throughout the length thereof a uniform cross-section.

The above aims of the invention are achieved by the combination of the two previously known methods described above. This is accomplished, according to the invention, by disposing a charge of the semi-conductor material in the form of a bar within a crucible, then causing the melting of a cross-sectional zone of the bar in the region adjacent the seed crystal, and transferring the molten zone at a constant rate of speed along the bar. During this transfer of the molten zone, the seed crystal and the new crystal portion adhering thereto are withdrawn from the melt at a constant rate of speed, such that the crystal withdrawn from the melt no longer contacts the walls of the crucible.

Due to the simultaneous withdrawal of the crystal and the transfer of the molten zone along the bar-shaped base material, it is possible to grow a single crystal having a substantially uniform diameter throughout its entire length. This surprising result is achieved by an automatic thermal control of the crystal growing procedure in carrying out the method of the present invention which may be explained as follows:

Despite constant withdrawal and crucible transfer speeds and constant heat supply, it is not possible to obtain a constant temperature at the surface of the melt. It is, therefore, important to consider the conditions resulting from such small temperature fluctuations occurring at the surface of the melt. If the temperature at the surface of the melt drops below a normal value, i.e., if the melt surface is somewhat colder, the diameter of

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the growing crystal will become larger. Since its withdrawal speed remains constant, it follows that the volume of molten material withdrawn from the melt during a given period will also be increased. This, in turn, causes the level of the melt surface to be lowered. The surface of the melt passes, therefore, into a region of higher temperature as it is displaced in a direction toward the center of the heating coil. Thereafter, the increase of temperature at the surface of the melt will result in a decrease of the diameter of the crystal withdrawn from the melt. From this, it appears that the fluctuation of temperature and the accompanying fluctuation in the diameter of the growing crystal at the surface of the melt is compensated by the fluctuation in the height of the melt surface and, consequently, the temperature prevailing at this place. The melt surface is constantly displaced into a hotter or colder region, so that the temperature fluctuations become equalized. The end result is that the fluctuation in the diameter, i.e., the size of the withdrawn crystal, is suppressed and the crystal obtained has a constant diameter throughout.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific example, while indicating the preferred embodiment of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

In the drawing:

FIGURE 1 illustrates schematically a longitudinal section through an apparatus for carrying out the method according to the present invention;

FIGURE 2 is a schematic showing on an enlarged scale of a longitudinal section through a part of the apparatus of FIGURE 1, illustrating the beginning of the withdrawing step;

FIGURE 3 is the same kind of showing as FIGURE 2, illustrating a later phase of the operation than that shown in FIGURE 2.

Referring in more detail to the drawings, FIGURE 1 shows a substantially conventional crystal growing apparatus for making crystalline and semi-conductors which was suitably modified for the purposes of the present invention. A crucible 1, which may be composed of carbon, graphite or quartz, or any other suitable material, is provided with a heating device, for example, a heating coil 2 surrounding the crucible 1 and causing the melting of only a portion of the material disposed within the crucible, when this heating coil is energized by a suitable source of electric current (not shown) connected to terminals 6 of the coil 2. The crucible 1 is provided with a charge of material which, because of the considerable axial length of the crucible, is in the form of a bar-shaped body 3. The material 3 is melted by means of the heating coil 2 in a relatively narrow region 4. A seed crystal 5, oriented in a particularly desired manner, is then immersed into the aforesaid molten region 4. As the operation described herein continues, the heating device 2, which maintains the melting zone 4 at a temperature preferably only slightly above the melting point of the material 3, is moved in the direction of the arrow at a speed  $v_s$ . The melting zone, the extent of which is usually held substantially constant, is thereby transferred slowly from one end of the body 3 to the other. At the same time, the seed crystal 5 is slowly withdrawn in the opposite direction at a speed  $v_k$ , so as to grow a crystal portion of molten material attached to said seed crystal and correspondingly oriented thereby.

In order to obtain the most uniform heat distribution in the melting zone 4 and, particularly, to have it independent of the geometrical position of the heating coil 2, it is preferred to have at least the seed crystal 5 or the crucible 1 with the charge 3 and 4 rotate about the axis 7. However, it is also possible to have both, the seed crystal 5 and the crucible 1, rotate in the same direction about this axis 7, i.e., at the same angular velocity, since, by this expedient, the growing crystal would be withdrawn from a melt apparently in the state of repose and the crystals resulting therefrom would be particularly uniform.

The inventive method is especially suitable for the production of crystals of mixed composition, as for example those consisting of a low melting component, hereinafter referred to as base material, and a higher melting component, which will be referred to as the addition material. In this connection, germanium, having a melting point of 930° C., is contemplated as base material for use with silicon as addition material, having a melting point of 1430° C. This addition material has a segregation constant greater than 1 in the melt. Therefore, the mixture will have a higher melting point or solidification point than the pure base material. In this regard, it is also contemplated to use addition which, in turn, may be composed of several single components.

In the preparation of crystals of mixed composition, it is preferable to use a seed crystal consisting of pure base material. This may be desirable for the reason that the melt, upon initiating the withdrawal procedure, is apt to depart in any event, as far as its composition is concerned, from the melt in the later stages of the melting procedure.

It is a particularly important advantage of the above system that it permits the withdrawal of a crystal of mixed composition and uniform growth in a single operation. This is especially difficult since the gradient of the addition material concentration in the withdrawn crystal body must be everywhere only of small magnitudes. If it is too great at a given point, the crystal body withdrawn would necessarily be polycrystalline in nature.

Preliminary to starting to grow such a mixed crystal, an initial zone of the bar consisting of pure base material is first melted and the crystal is then withdrawn therefrom. It is essential in carrying out the inventive method, that the temperature gradient within the melt extends from a maximum temperature in the center of the heating coil to a temperature at which the pure base material solidifies. The maximum temperature will be chosen in such a way that the liquid aggregate condition is maintained, even with the final composition of the melt.

After the seed crystal has contacted the surface of the melt and is withdrawn therefrom, the new crystal portion is caused to grow in the zone where the solidification takes place. The portion of addition material incorporated with the melt is now continuously increased from a zero value to a constant end value. This takes place because the melting zone passes from the initial zone which consists only of pure base material into the region of the bar that includes the aforementioned addition material. The increase of the portion of addition material in the melt is accompanied by an increase in its solidification temperature. Since the solidification region lies in the temperature gradient which includes the appropriate temperature range, this solidification region will be displaced along the gradient into the range of higher temperature where it adjusts itself in accordance with the solidification temperature varying according to the content of the addition material. This will insure the most efficient crystallization.

After passing through the intermediate zone, the mixed crystal will continue to grow at a constant rate which is

accomplished by the incorporation of addition material in constantly uniform amounts based upon the diameter of the base material body. Moreover, it is important that the withdrawal speed, displacement of the crucible and heat output be maintained constant. There is, of course, no particular problem in maintaining a mechanical movement constant. However, special care has to be taken to maintain the heat output at a constant value. For this reason, such values are preferably adjusted in the initial melting zone for the pure base material and at the beginning of the withdrawal operation. This will compensate for irregularities and changes in the temperature distribution encountered in the withdrawal of the mixed crystal portion proper. Thus, at the beginning the melt volume is somewhat larger, since the level of the melt will extend along the temperature gradient beyond the heating coil.

A preferred way of incorporating the addition material is to introduce it through a bore or like opening hollowed out of the base material bar, as shown in the examples in FIGURES 2 and 3 of the drawing. No addition material is present in the initial melt zone. With a view to obtaining a continuous transfer of the melt composition in the intermediate zone, the addition material will be present in the semi-conductor bar in the form of a cone.

FIGURE 2 shows the beginning of the withdrawal operation in the case of a mixed crystal. The crucible 1 is again surrounded by a heating coil 2 which is to melt only a certain zone of the crucible content. The material to be melted is placed in the crucible 1 in the form of a bar-shaped body 3 consisting of base material. This body, which has a cylindrical bore having a pointed head, contains a rod-like body 8, consisting of addition material, inserted in said bore. At the beginning of the withdrawal operation, the initial melting zone consisting of pure base material 4 is caused to melt. It will further expand, due to the low melting point of the base material, and extend somewhat beyond the heating coil 2 into a colder region where, at its melting temperature, the seed crystal 5 is applied. The highest temperature prevails at the center of the heating coil 2. It decreases in the direction of the axis of the crucible 1 which coincides with the direction of withdrawal.

FIGURE 3 shows the continuation of the withdrawal operation after the stationary condition is achieved. The solidification region has now passed into a hotter zone and the mixed crystal 5 will grow in this zone. In the melting zone, the constant heat output and the constant movement will cause the melting of both the base material 3 and the addition material 8 at a uniform rate. The growth of the mixed crystal under such stationary condition is, therefore, necessarily homogeneous and gradient-free.

I claim:

1. A method for obtaining a single crystal from a melt with the aid of a seed crystal, comprising the steps of placing a semi-conductor starting material in the form of a bar in a crucible, melting said bar so as to establish a melting zone in the upper cross-sectional region of the bar, contacting said upper cross-sectional region of the bar with a seed crystal, moving said melting zone downwardly along said bar at a constant speed, and withdrawing said seed crystal by moving the same upwardly at a constant speed together with a new crystal portion adhering thereto, said withdrawal of said crystal being concurrent with the movement of said melting zone, whereby the crystal withdrawn from the melt is out of contact with the walls of the crucible.

2. A method according to claim 1, characterized in that the heat output is maintained at a constant value during the withdrawal operation.

3. A method according to claim 1, characterized in that for the purpose of obtaining a mixed crystal the composition of the melt is continuously modified dur-

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ing the withdrawal operation by the successive incorporation of an addition material.

4. A method according to claim 1, wherein between the seed crystal and the melt at least one is caused to rotate about its longitudinal axis.

5. A method according to claim 3, wherein the addition material necessary for obtaining a mixed crystal is incorporated in said bar-shaped starting material in the form of a solid rod-shaped body having a pointed head and located below the initial upper end of said bar, whereby the end of said addition material lying in the direction of the melting zone has a diameter which continuously decreases until it reaches zero.

6. A method according to claim 3, wherein the addition material is incorporated in said semi-conductor bar below the initial upper end of said bar, whereby the melted zone at the beginning of the withdrawal operation is free of addition material.

7. A method according to claim 3, wherein said addition material is fitted into an opening provided in said semi-conductor bar.

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8. A method according to claim 3, wherein the dissociation coefficient of said addition material with respect to the base material is greater than 1.

9. A method according to claim 3, wherein between the seed crystal and the melt at least one is caused to rotate about its longitudinal axis.

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