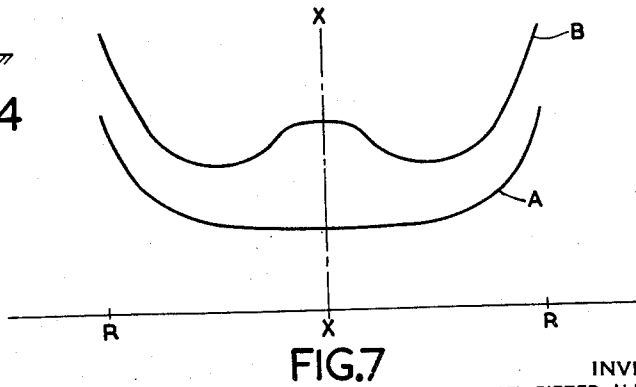
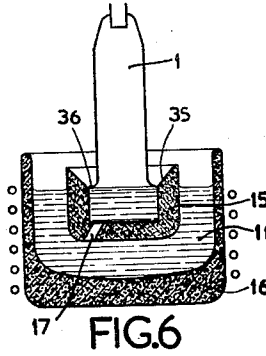
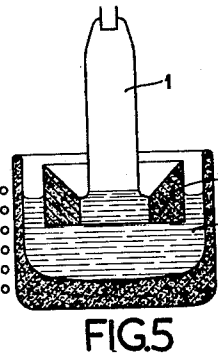
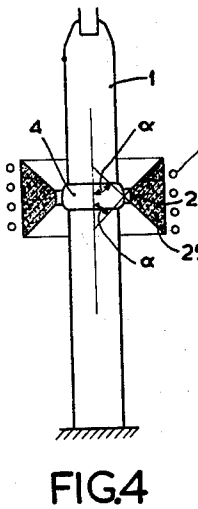
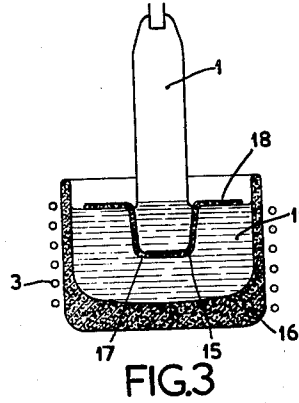
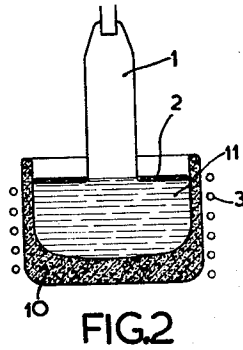
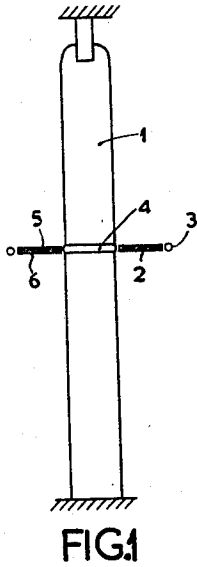


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METHOD AND APPARATUS FOR THE MANUFACTURE OF
CRYSTALLINE SEMICONDUCTORS
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METHOD AND APPARATUS FOR THE MANUFACTURE OF CRYSTALLINE SEMICONDUCTORS**Marcel Pieter Alfons François, Brussels, Belgium, assignor to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware****Filed Nov. 18, 1957, Ser. No. 697,046****Claims priority, application Netherlands Nov. 28, 1956****10 Claims. (Cl. 23—301)**

The invention relates to methods and apparatus for the manufacture of single crystals from a substance, for example a semi-conductor, such as germanium or silicon, in which by supplying heat from outside and/or by thermal excitation inside the substance by means of a high frequency electric field, a melt of this substance is produced, from which a single crystal is made to grow in a given direction in the form of a circular-cylindrical rod. In a further production stage this rod may be divided into smaller bodies; for instance in the case of a semi-conductive substance, these smaller bodies are used in semi-conductive devices, such as transistors or crystal diodes.

For producing mono-crystalline, semi-conductive rods several methods are known, inter alia drawing a single-crystal upwards from a melt in a crucible. An alternative method is zone-leveling, in which in an elongated boat containing a single crystal at one end and otherwise filled with poly-crystalline material, a narrow liquid zone is moved lengthwise of the boat starting from the single crystal side, and finally the zone-floating process, according to which a narrow liquid zone is moved lengthwise along a vertical rod starting from a mono-crystalline side of the rod onwards. Mono-crystalline rods produced according to these known methods suffer from a comparatively high content of dislocations which, moreover, are unevenly distributed over the cross-sectional area of the rod. These dislocations adversely affect the physical properties of the single-crystal, for example its conductivity, and their uneven distribution over the cross-sectional area may constitute a disturbing factor in the further processing of the single crystal, for example in diffusion or alloying.

It is known that the dislocations arise for the major part after crystallisation due to thermal stresses inside the freshly grown mono-crystalline rod when being at a high temperature. It is also known that thermal stresses in a circular-cylindrical rod are due to radial heat losses inside the rod and are avoided by maintaining a constant temperature gradient in the rod along its axis.

In zone leveling it has been proposed to prevent radial heat losses by maintaining the grown, mono-crystalline rod as a whole at a temperature only a little below the melting temperature of the rod, and by cooling the whole rod slowly and evenly after termination of the growing process. In said device, this tempering of the grown rod at elevated temperature is effected by means of a high frequency coil heating an elongated graphite cylinder which surrounds the boat. This coil consists of two parts, namely a part having a small pitch for producing the molten zone and a contiguous part of greater pitch by which the graphite cylinder is locally heated sufficiently to maintain this grown, mono-crystalline rod as a whole at a substantially constant temperature a little below its melting temperature.

Apart from the cumbrousness of this method it suffers from the disadvantage of taking considerable time due to the low temperature gradient at the solid-liquid interface, which low temperature gradient involves a slow growth. Moreover this method merely constitutes a shift of the difficulty to a later stage, in which the rod still being substantially at its melting temperature is slowly and evenly

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cooled as a whole. Moreover, this method is practicable only in zone leveling, a method which in itself is least suitable, due to dissymmetry of the required apparatus, for the production of mono-crystalline rods free from stresses and dislocations.

The present invention has for its object to provide a method in which this problem is solved fundamentally without involving the aforesaid disadvantages by maintaining, in that part of the grown mono-crystalline rod where thermal stresses might involve dislocations, a constant temperature gradient which prevents thermal stresses and concomitant dislocations.

In the method according to the invention, the loss of heat during the growing process due to radiation at the surface of that portion of the grown single crystal rod, which has a high temperature exceeding the softening temperature of the substance, is compensated by inward radiation of heat from an external heat radiating member which is arranged symmetrically around the axis of the rod and the geometry and the temperature distribution of which are so chosen as to compensate at least partly, but as completely as is practically feasible, for any heat radiated from any one surface element of said portion having the desired constant temperature gradient. The term "softening temperature" of a material is to be understood to mean the lowest temperature at which dislocations are still produced by thermal stresses inside this material. The softening temperature of germanium and silicon is approximately 400° C. and 800° C. respectively. The invention particularly applies to the two known methods in which cylinder-symmetrical apparatus are used. For these cases the invention delivers two particular examples of radiation members, of which the geometry is so chosen that the radiation member is to be held at a practically constant temperature.

The invention is based on the realisation that in such a circular-cylindrical rod a constant temperature gradient can be maintained by completely compensating the radiation from the surface at this temperature gradient, that is to say by compensating it in such manner that the resulting heat current through any arbitrary surface element is zero. It further takes advantage of the recognition that at least in a finite portion of the grown, single crystal rod, namely that portion the temperature of which exceeds the softening temperature, substantially complete compensation is obtainable in a simple manner only by inward radiation of heat from a source of thermal energy, for example a ring having a suitable geometry and temperature distribution.

The term "complete compensation" is to be understood in a wide practical sense. Theoretical complete compensation is, of course, unfeasible in practice but can be closely approximated, as in the particular forms of the method according to the invention referred to later.

In a particularly suitable form of the method according to the invention, a heat radiating member is employed which consists of a ring extending coaxially of the rod and being contiguous with the solidification surface, it accommodating the rod with a little clearance and its outside diameter corresponding to or exceeding at least twice the diameter of the rod, while its side facing the grown single crystal rod is flat and has a constant or substantially constant temperature at least corresponding to the melting temperature of the rod. It is of paramount importance for the radiation ring to approach the rod as closely as practically possible without touching it, since it is the nearby parts of the ring which contribute appreciably to said compensation. From theoretical considerations it has further been found that practically ideal compensation at a given temperature gradient inside the rod is obtainable by choosing a given ratio of the outside diameter and the inside diameter. In practice, excellent results

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are obtained if this ratio is between 2 and 3, in other words if the outside diameter of the radiation ring is twice to three times the diameter of the rod, it being further pointed out that the width of the ring, that is to say half the difference between the outside diameter and the inside diameter, is made larger as the temperature gradient is lower. Instead of matching the size of the ring to the temperature gradient it may sometimes be advantageous, by cooling the rod portion already having a temperature lower than the softening temperature, to match the temperature gradient to the size of the ring, preferably by cooling at a fixed distance from the radiation ring, thus invariably maintaining a constant temperature gradient forced by cooling.

The effect obtained by the invention is also secured when using a heat radiating member consisting of a radiation ring coaxial with the rod and the inner side of which, at least that part surrounding the solidification surface and a contiguous grown mono-crystalline rod portion having a temperature in excess of the softening temperature, tapers conically in a direction corresponding to the direction of growth of the rod and has a substantially constant temperature corresponding at least to the melting temperature of the rod. It is not necessary for this conical radiation ring to surround the rod closely, at variance with the flat ring referred to. The slope of the conical part, that is to say the angle subtended by the generatrix of this conical part and the axis of the rod advantageously exceeds 30° and preferably amounts to 40° to 50°.

The radiation ring is preferably made from conductive material having as high a radiation coefficient as possible. It preferably consists of graphite.

In order that the invention may be readily carried into effect, examples of this method and a form of the apparatus used for carrying it out will now be described in detail with reference to the accompanying drawing, in which:

FIGS. 1 and 4 represent schematically in cross-section two apparatus according to the invention intended for the floating zone technique.

FIGS. 2, 3, 5 and 6 are sectional views of forms of an apparatus according to the invention for pulling up a single crystal rod.

FIG. 7 is a graph indicating the etch pit density as a function of the distance from the axis for a rod made by means of an apparatus as shown in FIG. 2, and for a rod produced in known manner without having recourse to a radiation ring.

FIG. 1 shows schematically an apparatus according to the invention for use in zone-leveling without a crucible. A vertical, freely arranged elongated rod 1, for example consisting of silicon, is locally surrounded by a disc 2 of graphite, the outside diameter of which is twice to three times as large as the diameter of the rod. The graphite ring 2 is heated by means of a high-frequency field produced by a high-frequency coil 3. Due to thermal radiation from the inner side of the graphite ring 2, a narrow liquid zone 4 is formed and maintained in the rod, which zone is movable lengthwise of the rod, for example by vertical displacement of the graphite ring 2 and the high-frequency coil 3. The thickness of the ring 2 is determined by the amount of heat required for melting the zone. The graphite ring accommodates the rod 1 with a little clearance so that neither the melt nor the rod is touched by the ring. From a mono-crystalline end onwards, for example the top of the rod, the radiation ring 2 is moved downwards and the mono-crystalline rod grows in this direction. As a result of thermal radiation from the flat upper side 5 of the ring 2 into a part of the grown rod, for example within a distance corresponding to the diameter of the rod above the solidification surface, the heat radiated at a constant temperature gradient into this part, can be compensated completely. Since the ring 2 has a rectangular cross-sectional area, the growth may

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alternatively occur in the opposite direction, so that the flat lower side 6 of the ring fulfills the compensating function.

Upon calculation it is found that perfectly ideal compensation is obtainable by heating a radiation ring, which extends right to the rod and has a radiation coefficient ϵ , to a temperature corresponding to

$$\sqrt[4]{\frac{2}{\epsilon}} T_{sm}$$

where T_{sm} represents the melting temperature of the rod in degrees Kelvin. For a graphite radiation ring having a radiation coefficient of approximately unity, this consequently means a temperature of $\sqrt[4]{2} T_{sm} = 1.19 T_{sm}$. Since ideal circumstances do not occur in practice, a slightly higher temperature is used, namely 1.2 to $1.5 \times T_{sm}$. In general, it may be assumed that the radiation ring, when heating it to such a high temperature as to form the molten zone under the action of its thermal radiation, also has the temperature desired in connection with ideal compensation.

The apparatus according to the invention which is diagrammatically shown in FIG. 2, is suitable for drawing a mono-crystalline rod upwards. A crucible 10, for example consisting of graphite, contains a melt 11 of germanium and is heated by means of a high-frequency electric field produced by the high-frequency coil 3. Through the aperture of a graphite ring 2 floating on the melt 11 a single crystal rod 1 having a diameter corresponding, but for a little clearance, to the inside diameter of the ring is drawn upwards. The upper side of the ring acts as a heat-radiation compensating wall. The portion of the rod inside the graphite ring 2 is practically still in the molten state. In order to avoid interruption of the contact between the rod and the melt in pulling up, the radiation disc is preferably less than 5 millimetres thick. Since the crucible wall of graphite shields the high-frequency electric field efficiently from the radiating ring 4, the latter is substantially heated indirectly, namely by the melt. Hence, the radiation ring has a temperature corresponding to or only slightly exceeding the temperature of the melt. This yields no ideal compensation, it is true, but at least a great improvement upon the known method without using an additional radiation ring. In the absence of the radiation ring, the surface of the melt acts as a compensating heat-radiation member. In practice, this compensation proves to be inadequate due to the low radiation coefficient of the molten material. By increasing the coefficient of the heat-radiation surface, in the present case by using a floating graphite ring, said compensation is greatly improved. Increasing the radiation coefficient of the radiation member is tantamount to increasing the temperature of the radiation member. According to the invention, the temperature of the radiation ring may be further increased by providing the upright walls of the crucible 10 with incisions of such a small width, for example 0.25 mm., as to prevent the melt, owing to its surface tension, from flowing out of the crucible through these incisions. In this case, a relatively larger part of the high frequency field is allowed to penetrate to the radiation disc and to heat it instantly.

According to the invention the temperature of the floating radiation ring may be increased to exceed the melting temperature when using a crucible of insulating material, for example a quartz crucible, in combination with a radiation ring of conductive material, for example a graphite ring. In this case also the radiation ring is directly heated by means of the high-frequency field, and formation of the melt may be initiated and controlled by the heat radiated from the radiation ring.

The two last-mentioned steps according to the invention have a further advantage in that the vertical up-standing wall of the melting crucible is heated only to a comparatively low temperature, so that the amount of radiation reaching the surface of the mono-crystalline

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rod and interfering with the desired radiation pattern is reduced. As a matter of fact, the considerations on which the present invention is based have also led to the recognition that a vertical radiation wall, for example the conventional high, narrow radiation ring used in zone leveling and the inside diameter of which considerably exceeds the rod diameter, or the crucible wall overtopping the melt upon drawing the rod upwards, yields a radiation pattern greatly different from the desired radiation compensation. These differences particularly occur at the most delicate part of the rod, namely the part immediately contiguous of the liquid-solid interface. Therefore, radiation from such a wall should be limited as much as possible.

FIG. 3 shows diagrammatically an apparatus in which the invention is applied to a known apparatus for drawing mono-crystalline rods upwards. This apparatus permits a mono-crystalline rod to be made having a substantially constant specific resistance in a longitudinal direction. The mono-crystalline rod 1 is lifted from a crucible 15 which floats in the melt 11 of a larger crucible 16 which is connected through an opening 17 with the melt 11 of the larger crucible 16. The liquid levels in both crucibles are the same or substantially the same. According to the invention the floating crucible 15 comprises a flat edge 18 preferably having the width referred to above, the upper side of which constitutes the compensating radiation surface, while its lower end rests on the melt 11 so that the liquid level inside the crucible extends approximately to the flat edge, the crucible (15, 18) being of such a size, or the pull rate of the mono-crystalline rod being so adjusted that the diameter of the mono-crystalline rod corresponds, but for a little clearance, to the inside diameter of the flat edge of the crucible.

FIGS. 4, 5 and 6 show apparatus according to the invention, in which the external heat-radiating member is constituted by a radiation ring co-axial with the rod and the inner side of which, at least the part surrounding the surface of solidification and a contiguous grown mono-crystalline rod portion having a temperature exceeding the softening temperature, tapers conically in the sense corresponding to the sense of growth of the rod. When using the method according to the invention, the radiation ring is heated to such a high substantially constant temperature that the plan of solidification lies within the conical part of the radiation ring.

FIG. 4 shows an apparatus according to the invention, intended for zone melting without using a crucible. The vertical rod 1 is surrounded by a radiation ring 25 having a cross-section in the form of a trapezium, the shorter parallel side 26 of which faces the rod 1. The ring comprises an inner cylindrical part between its two parts extending conically towards the melt. The generatrices of the two conical parts subtend an angle α of approximately 45° with the axis of the rod. When heating the graphite ring 25 by means of the high-frequency coil 3, a molten zone 4 is produced in a rod 1, which zone extends into the conical parts. On lowering the radiation ring 25 and the high-frequency coil 3 the rod grows mono-crystalline from top to bottom and the upper conical part acts as a compensating heat radiation ring. During the upward movement the rod grows from bottom to top and the lower conical part acts as a compensating heat-radiation ring.

In the apparatus according to the invention represented diagrammatically in cross-section in FIG. 5, which is intended for pulling up a mono-crystalline rod, a radiation ring floating on the melt is used similarly as in the device shown in FIG. 2. This radiation ring 30 comprises a conical part flaring in the direction of growth of the rod i.e. in the direction of the melt, which part passes over into a cylindrical part. In the method according to the invention, the radiation ring is kept floating so that only a conical part extends above the melt.

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The device shown in FIG. 6 is analogous to the device shown in FIG. 3, but in FIG. 6 the said upper edge 18 of the crucible 15 shown in FIG. 3 is replaced by a conically tapering inner wall. Such a device which comprises a crucible 15 whose inner wall 35 tapers conically at least at its upper edge and which floats on the melt 11 of a larger crucible 16 and is connected therewith through an opening 17 is known per se. According to the invention, however, the crucible 15 is kept floating in the melt so that only a conically tapering inner wall extends above the liquid level 36 of the crucible. In this manner the lifted rod 1 is subject to radiation only from the conical inner wall.

It is to be noted that the steps described with reference to FIG. 2 for increasing the temperature of the floating radiation ring may also be used to great advantage in the devices shown in FIGS. 3, 5 and 6.

The effect of the invention will be more fully explained with reference to FIG. 7 which is a graphical representation of the results obtained by means of the device and the method illustrated in FIG. 2. The density of the etch pits per cm^2 in arbitrary units is plotted vertically. This density is a measure of the dislocation density inside the crystal, while the distance from the axis X—X of the rod, which axis is indicated in broken lines, is plotted horizontally.

The curve A represents the etch pit distribution over the cross-sectional area of a mono-crystalline rod obtained by means of the method and device shown in FIG. 2. The curve B illustrates the etch pit distribution of a mono-crystalline rod pulled up without using a radiation ring. It is obvious that with the mono-crystalline rod obtained when using a method according to the invention the etch pit density is lower and the etch pits are distributed more evenly over the cross-sectional area, the etch pit density still increasing considerably only at the edge of the rod. In this connection it is pointed out, however, that the temperature of the floating radiation ring was lower than that required for ideal compensation. In spite thereof the improvement obtained was appreciable.

What is claimed is:

1. Apparatus for growing, by crystal cylindrical pulling, a single crystal semi-conductive rod, comprising a crucible for holding a quantity of molten semi-conductive material, a heating coil surrounding the crucible for adding heat thereto, an annular heat radiator within the crucible and contacting the melt, means for drawing molten material up through the opening in the radiator to cause same to solidify into a rod whose diameter is just slightly less than the diameter of the radiator opening, said radiator having a high radiation coefficient and a high radiating surface at the melt surface, and means for maintaining said radiation at a temperature at least equal to that of the melt to cause the just-grown rod to receive radiant heat therefrom to compensate for its own heat loss and thus improve the quality of the grown rod.

2. Apparatus as set forth in claim 1 wherein the radiator is of graphite and has a flat surface extending parallel to the melt surface.

3. Apparatus as set forth in claim 1 wherein the radiator is of graphite and has a conical surface.

4. Apparatus for growing a single crystal cylindrical semi-conductive rod, comprising a crucible containing semi-conductive material, a high-frequency heating coil surrounding the crucible for melting the semi-conductive material therein, an annular disc-like heat radiator having a circular opening and a relatively high radiation coefficient and having an outwardly extending heat-radiating surface at the melt surface, means for pulling a growing single crystal from the melt up through the annular radiator so that the rod diameter is slightly smaller than the inner diameter of the annular radiator, and means for maintaining said radiator at a temperature at least equal to that of the melt, thereby to radiate heat to the

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just-grown portion of the rod to compensate for its own heat loss and thus to improve the quality of the grown rod.

5. Apparatus as set forth in claim 4 wherein a small, apertured crucible depends from the heat radiator.

6. Apparatus as set forth in claim 4 wherein the crucible is of conductive material and contains slots in its wall to limit the flow of high-frequency heating currents therein.

7. Apparatus as set forth in claim 4 wherein the crucible is of insulating material and the heat radiator is of conductive material.

8. Apparatus for growing, by crystal pulling, a single crystal semi-conductive rod, comprising a large crucible for holding a quantity of molten semi-conductive material, a heating coil surrounding the crucible for adding heat thereto, an annular heat radiator with an inner, outwardly-tapered radiating surface within the crucible and floating on the melt such that only the tapered surface extends above the melt, and means for drawing molten material up through the opening in the radiator to cause same to solidify into a rod whose diameter is just slightly less than the diameter of the radiator opening, said radiator having a high radiation coefficient, and means for maintaining said radiator at a temperature at least equal to that of the melt to cause the just-grown rod to receive radiant heat therefrom to compensate for its own heat loss and thus improve the quality of the grown rod.

9. Apparatus as set forth in claim 8 wherein a small apertured crucible depends from the annular heat radiator.

10. A method for growing a single crystal in the form

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of a substantially cylindrical rod from a semiconductive melt, comprising providing in contact with the melt an apertured annular member whose inner diameter is only slightly greater than the rod diameter to be grown and whose outer diameter is at least twice the said rod diameter and having a high radiation coefficient, contacting the melt through the aperture in the annular member with a single crystal, drawing the single crystal upwards through the apertured annular member so that the grown rod just fills the aperture, and maintaining said annular member at a temperature at least equal to that of the melt thereby radiating heat to the just-grown rod portion contiguous with the molten zone, thereby to improve the quality of the resultant single crystal.

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