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Keller et al.

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[54] **PREPARING ORIENTED SEMICONDUCTOR MONOCRYSTALLINE RODS**

[75] Inventors: **Wolfgang Keller; Alfred Muehlbauer**, both of Munich; **Konrad Reuschel**, Vaterstetten, all of Germany

[73] Assignee: **Siemens Aktiengesellschaft**, Berlin & Munich, Germany

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[51] **Int. Cl.²** **B01D 9/00**; B01J 17/20

[58] **Field of Search** .... 23/301 SP, 273 SP

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Primary Examiner—Norman Yudkoff
Assistant Examiner—Darrel Sanders
Attorney, Agent, or Firm—Hill, Gross, Simpson, Van Santen, Steadman, Chiara & Simpson

[57] **ABSTRACT**

A process for preparing oriented semiconductor monocrystalline rods with a specific resistance which drops towards the center of the rod. The process utilizes rapid non-crucible moving zone melting of a preformed vertically positioned semiconductor rod using an inductive heating device which annularly surrounds the rod.

8 Claims, 5 Drawing Figures

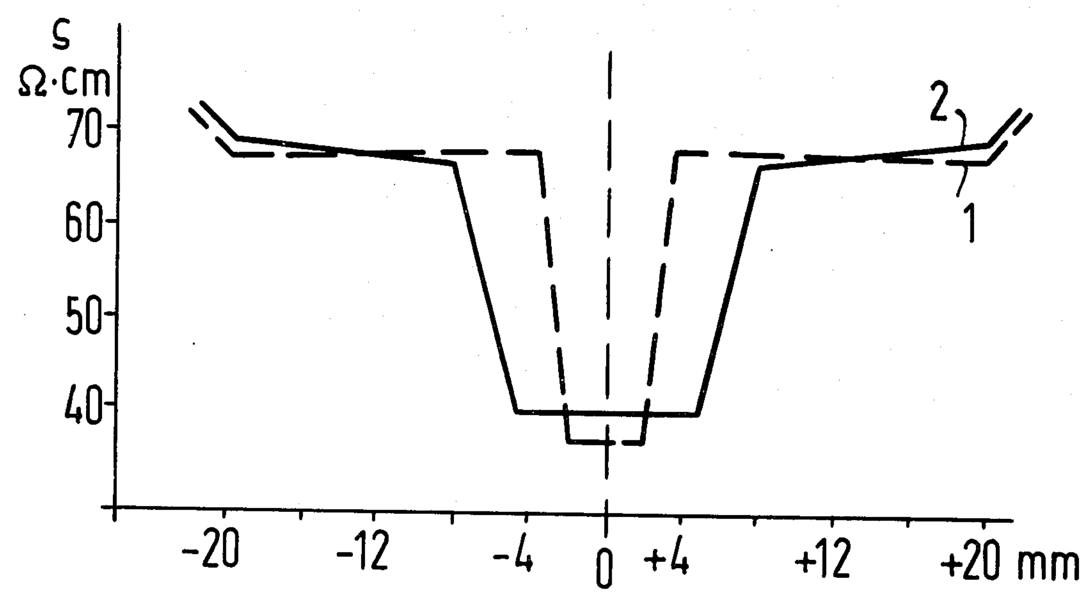
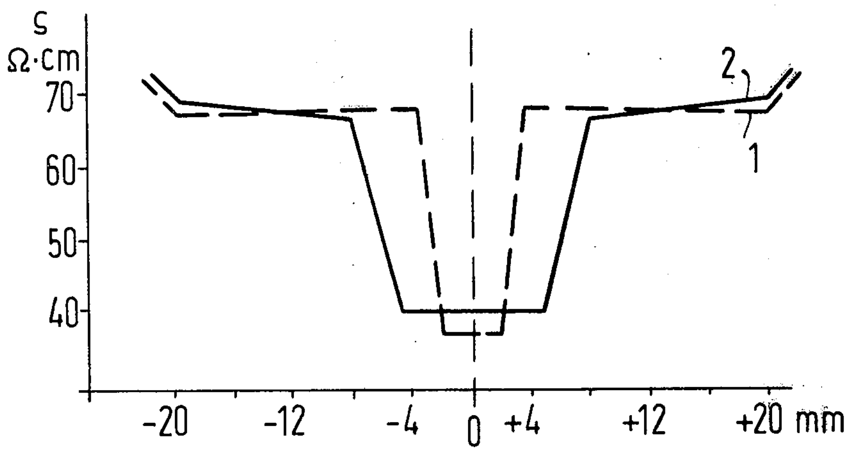


Fig.1


ς
Ω·cm
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60
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40
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1
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-12
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+4
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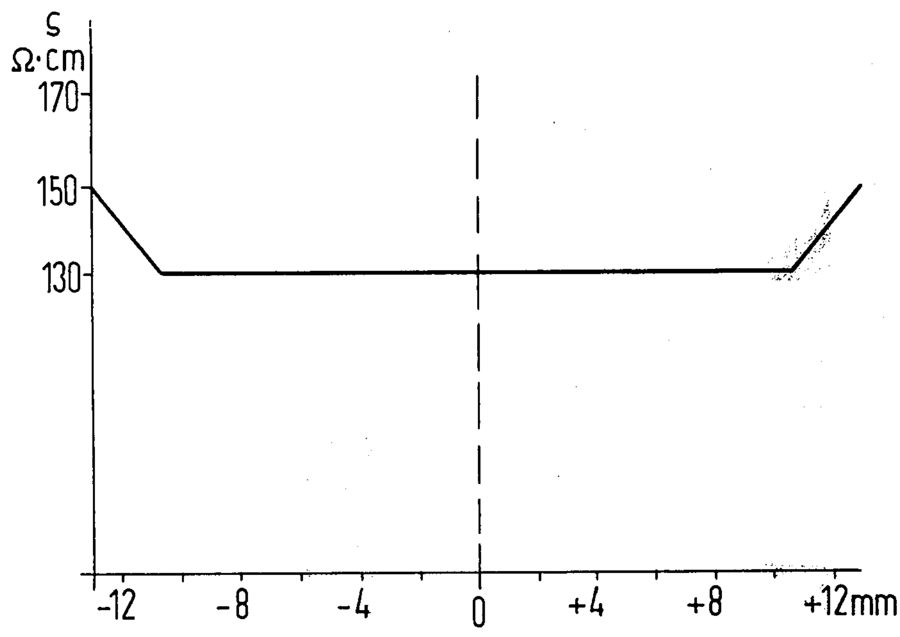
+20 mm

Fig.2


ς
Ω·cm
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150
130
-12
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-4
0
+4
+8
+12mm

Fig.3

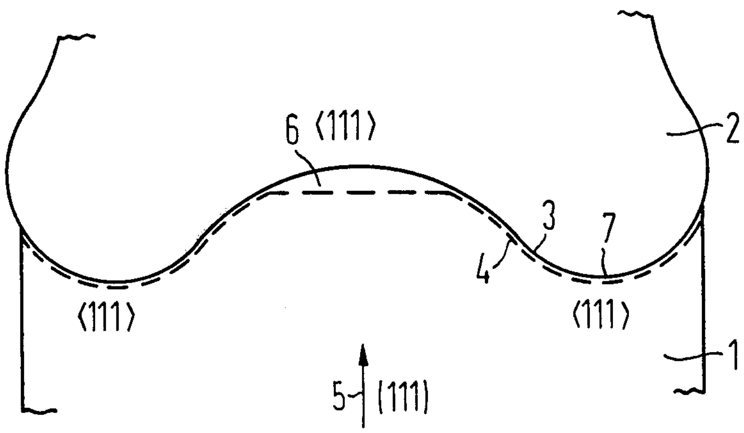


Fig.4

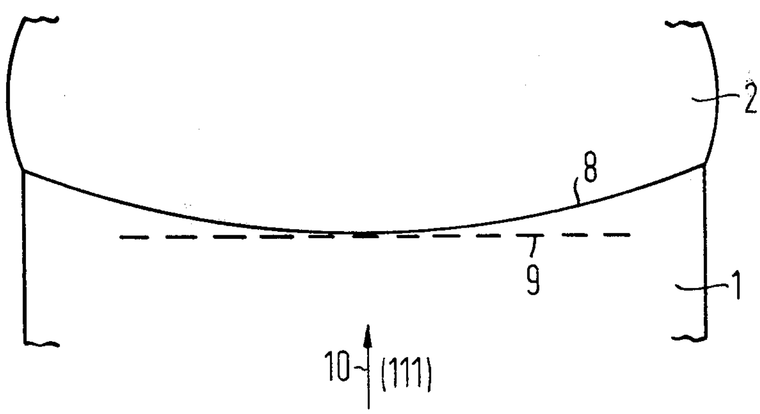
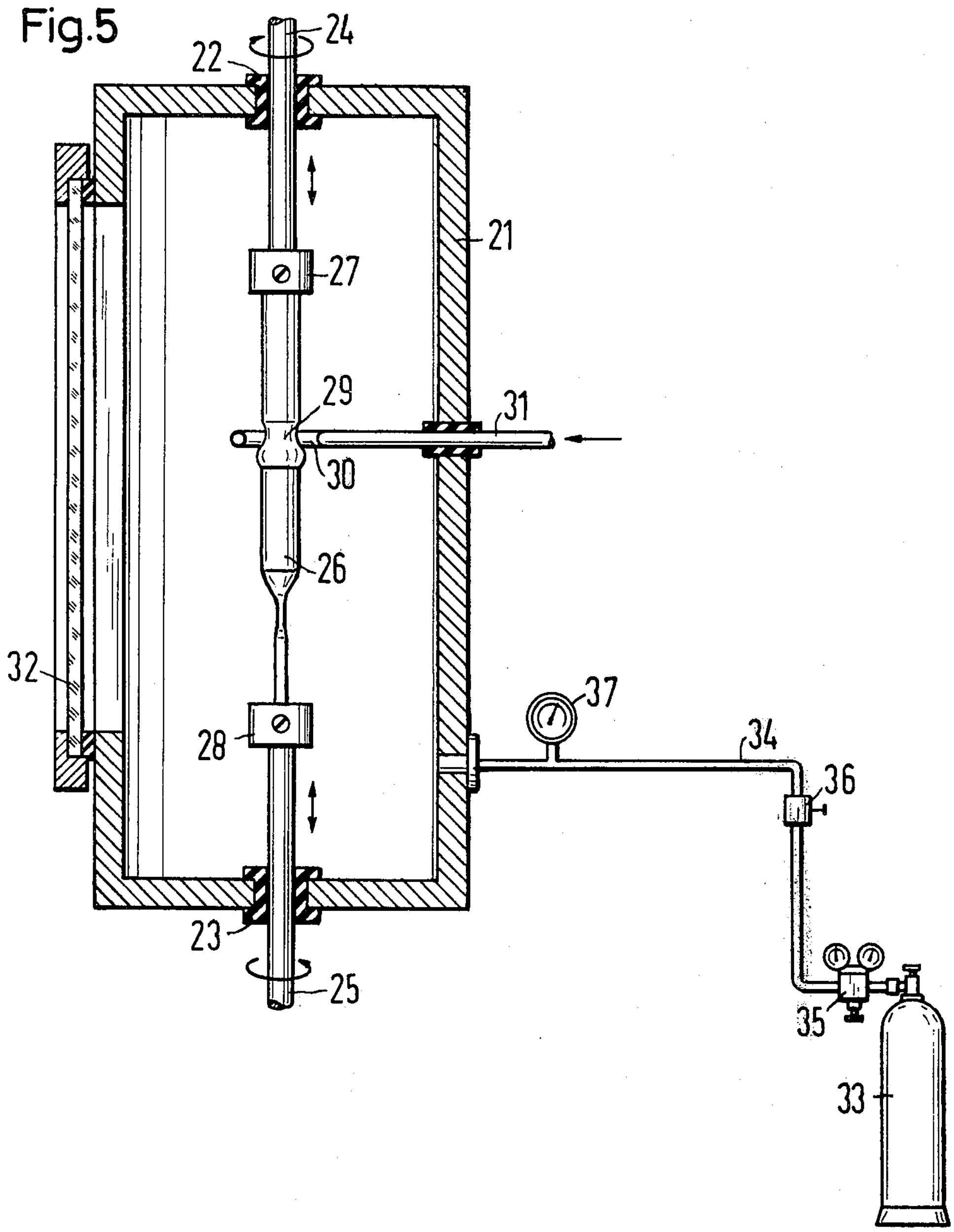


Fig.5



PREPARING ORIENTED SEMICONDUCTOR MONOCRYSTALLINE RODS

BACKGROUND OF THE INVENTION

Monocrystalline rods have been produced by non-crucible zone melting with the aid of seed crystals by heating preformed, doped polycrystalline semiconductor rods, in particular silicon rods. A molten zone is made to travel longitudinally and circumferentially from one end of a preformed polycrystalline semiconductor feed rod section where a seed crystal is applied to the other end thereof. In this process, the semiconductor rod is generally fixed vertically between two holders, and at least one holder is set in rotation about the rod axis during such zone melting, thus ensuring a symmetrical growth within the solidifying material. Generally, in this process it is desirable to produce monocrystalline rods for the manufacture of semiconductor components which possess very uniform values in terms of their specific resistance measured radially from the rod center outwardly, or vice versa. Thus, a very thorough mixing of the melt is achieved during such non-crucible zone melting in order that the distribution of the dopant within the rod takes place as homogeneously as possible over a cross-section of the crystalline rod (e.g. silicon).

For the production of semiconductor material to be used for the manufacture of special semiconductor components, for example, thyristors which may be ignited in overhead fashion, one preferably employs as the semiconductor basic material (**111**)-orientated silicon crystalline wafers, which each possess a deliberate break or change in the specific electric resistance (ρ) in their center. For certain other power components, it is advantageous, for example, to have a homogeneous ρ-course in the center of the wafer and to have a deliberate border or side increase in ρ relative to the center thereof. As those skilled in the art appreciate, such wafers are conveniently and conventionally formed by transversely slicing a suitable preformed semiconductor monocrystalline rod.

BRIEF SUMMARY OF THE INVENTION

The present invention has as a primary aim the provision of a resistance profile in a semiconductor monocrystalline rod which varies radially from the rod central region outwardly, or vice versa. Such a profile is produced by non-crucible zone melting of a preformed, doped semiconductor monocrystalline rod, preferably comprising non-dislocated, (**111**)-orientated silicon monocrystals.

The present invention realizes this aim by providing a process in which a feed or starting monocrystalline cylindrical rod is selectively heated under controlled conditions to produce a monocrystalline rod of smaller diameter which has a desired such resistance profile. A melt zone rapidly moving through a rod is used.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. **1** shows the resistance profile associated with an overhead ignitable, ignition resistant thyristor;

FIG. **2** shows the resistance profile associated with a high power diode;

FIG. **3** is a partial, vertical sectional view through a silicon rod being zone heated and rotated in accordance with the teachings of this invention but not subjected to a moving zone of heat, this FIG. illustrating a characteristic solid-fluid phase boundary profile so produced in such rod, which profile, in a product semiconductor wafer member, results in a resistance profile as illustrated in FIG. **1**;

FIG. **4** is a vertical sectional view through another silicon rod, but of the type shown in FIG. **3**, which not only is being heated and rotated as in FIG. **3**, but also is being subjected to an axially rapidly moving zone of heat, this FIG. illustrating the desired solid-fluid phase boundary profile so produced in such rod, achievable in the practice of the present invention, which profile, in a product semiconductor wafer member, results in a resistance profile as illustrated in FIG. **2**; and

FIG. **5** illustrates an embodiment of one form of apparatus suitable for use in the practice of the present invention.

DETAILED DESCRIPTION

The present invention is directed to a process for the production of (**111**)-orientated semiconductor monocrystalline rods with a specific resistance which drops towards the center of the rod. This process employs non-crucible zone melting of a preformed, initially polycrystalline, starting or feed semiconductor rod held vertically at its opposite ends. Such a zone melting is achieved by using a zone of heat annularly surrounding such rod, such zone being produced by an inductive heating device or the like which surrounds a portion of the rod circumferentially and concentrically and which produces within the adjacent encircled rod portion the desired melt zone. One end of the starting rod is contacted with a seed crystal, and, commencing from such end, the melt zone is longitudinally relatively moved through the semiconductor crystalline rod in the direction of the rod axis, such movement being achieved by spacially moving the rod relative to the heat zone, or vice versa, or by using some combination thereof. Simultaneously, the rod is revolved axially. As the melt zone cools, there is produced a monocrystalline rod which has a smaller diameter than the feed rod.

The movement of the melt zone through the rod is termed "pulling" or "drawing," and, in the present invention pulling is carried out at a relatively rapid speed. A constantly concavely curved boundary area is produced at the solid-fluid phase boundary in the rod undergoing such zone melting to which boundary a (**111**)-tangent can be applied only in the center of the rod.

In the process of this invention, the drawing (or pulling) speed of the melt zone is at least about **3.5** mm/min, and preferably a drawing (pulling) speed of about **5.5** mm/min is used. During such drawing (or pulling) the axial displacement of rod material is set to be less than about 10 percent of the diameter of the semiconductor monocrystalline rod which is to be produced. The ratio of the diameter of the feed rod to the diameter of the product monocrystalline rod is adjusted to be not less than about **1:1**, and preferably is greater than about **1:1**.

When the product monocrystalline rod is conventionally sliced into wafers, the wafers display specific resistance profiles which drop towards the wafer center. Thus, a characteristic, exemplary silicon wafer resistance profile achieved through the production of silicon rods by the teachings of this invention is shown in FIG. **2** which involves non-dislocated, (**111**)-orientated silicon monocrystals. FIGS. **1** and **2** show resistance profiles which are used for overhead-ignition-resistant thyristors (FIG. 1) and for high power diodes (FIG. 2). The specific electric resistance ρ is plotted in Ohm. cm. as ordinate, and the radius of the crystalline wafer is plotted as abscissa. The broken line which runs in parallel to the ordinate indicates the center of the wafer.

The following considerations represented in FIG. 3 led to the process of the present invention: During the drawing of (111)-orientated silicon crystals with a phase boundary which is convexly curved to the melt, a (111)-facet is formed, especially when a rod is concentrically drawn (e.g. the melt zone is maintained in a uniform condition with uniform, radially symmetrical dimensions as it is moved through a rod). This facet, which is characteristically located in the center of the rod, correspondingly becomes larger, the more undisturbed the growth of the crystal. The facet is particularly noticeable in the case of a non-dislocated silicon crystal due to the fact that, in the case of the crystal which exhibits non-dislocated growth, the degree of undercooling necessary for the formation of a crystallization seed on the facet is greater than in the case of dislocated silicon. The dislocations affect the (111)-facet almost in the manner of crystallization seeds before the drastic degree of undercooling characteristic of rods exhibiting non-dislocated growth has been reached. In dislocated silicon, the atom layer begins to advance laterally (horizontally) prematurely; in this case the facet is small.

It is further known that the dopant conventionally and characteristically in a starting rod is incorporated into the monocrystal of the product in a greater concentration in the region of the facet than outside the facet region which concentration gradient causes a break in the specific resistance of the rod in the region of this (111)-facet. Since, for example, thyristor silicon is mainly produced in non-dislocated form, the facet, and thus also the specific resistance break occuring in the facet region is particularly deep and of wide expanse.

In FIG. 3, a growing silicon monocrystal **1** is formed as the moving melt zone **2** solidifies. The line **3** indicates the course of the melt isotherms, and the line **4** indicates the solid-fluid phase boundary. The arrow **5** represents the direction of growth of the crystal in the (111)-direction. Frequently, a faceted inner region **6** which is convexly curved, relative to the boundary area, is accompanied at the edge by a ring-shaped concave region **7**. This concave region **7** is termed, in accordance with the main minimum in the ρ-profile occuring in the center of the rod, the secondary minimum ρ in the profile. It has been established that here, too, there is a dopant maximum concentration in the semiconductor material along the ring **7**. An aim of the present invention is to displace this dopant maximum located in the secondary minimum, and thus the concave region itself, into the center region of the rod, by influencing the form of the boundary area of the solid-fluid phase.

FIG. 4 shows the form of the solid-fluid phase boundary which is achieved by the practice of the process of the present invention. Here, the recrystallized, monocrystalline silicon rod **1** is continuously formed from the moving melt zone **2**. The line **8** shows the course of the boundary of the solid-fluid phase, and the horizontal line **9** represents the (111)-tangent which can be applied only in the center of the rod. The arrow **10** indicates the growth direction of the crystal in the (111)-direction, that is to say, when the seed crystal is arranged towards the bottom, the monocrystalline rod grows from below in the upwards direction.

Referring to FIG. **5** there is seen one form of apparatus suitable for the practice of the present invention, but those skilled in the art will appreciate that many different equipment forms may be used without departing from the spirit and scope of the present invention. Here, vessel **21**, which has defined therewithin an elongated, vertically oriented chamber, is provided in its top and bottom portions with passages equiped with respective annular seals **22** and **23** which ensure vacuum-tight passage therethrough of coaxial, longitudinally spaced drive shafts **24** and **25**. A crystalline rod **26**, which may be a polycrystalline silicon rod, or the like, is secured at its opposite ends in respective mountings **27** and **28**. The mountings **27** and **28** are fixed to the adjoining ends of the shafts **24** and **25**, respectively. The shafts **24** and **25** can be axially reciprocated and also rotated about their respective axes. A molten zone **29** is produced in the rod **26** by means of an electric induction heating coil **30** which is preferably an annular coil comprising a single winding. The induction heating coil **30** is fixed relative to vessel **21** and is passed in vacuum-tight fashion through a side wall of the vessel **21** by means of a mounting assembly **31**. The mounting assembly **31** can take the form of a coaxial mounting which is used both to supply the current and a coolant for the coil, preferably water. In the side wall of the vessel **21** generally opposite the mounting assembly **21**, an inspection window **32** is provided. Hydrogen, argon, or other suitable inert gas is fed from a reservoir **33** through a piping system **34** into the vessel **21**. In the piping system **34** there is provided a reducing valve **35**, a shutoff valve **36**, and a pressure gauge **37**.

The gas contained in the reservoir **33** is preferably a high-purity product. For example, by diffusion through palladium, and/or by freezing, it is a simple matter to purify hydrogen gas so that its purity is at least **99** weight percent. A purity of **99.999** weight percent is indeed readily attainable and is preferred for a gas used in this invention. The pressure in the vessel **21** is set to some convenient, predetermined value, for example, about **100** mm Hg in practicing this invention.

In the practice of this invention, as indicated above, the rod undergoing zone melting is rotated, for example, in the vessel **21** of the apparatus shown in FIG. **5**. Shaft **25**, when it holds the starting or feed rod portion, is revolved at a substantially uniform rate of from about **5** to **100** revolutions per minute (r.p.m.), preferably about **20** r.p.m., while shaft **24**, when it holds the recrystallized monocrystalline product rod, is revolved at a substantially uniform rate of from about **0** to **50** r.p.m., preferably about **5** r.p.m. The shafts **24** and **25** are preferably rotated in the same direction but these shafts may also counterrotate with respect to one another if desired.

As indicated above, the melt zone **29** moves vertically, preferably upwardly, at a substantially uniform rate of at least about **3.5** mm/min., and this speed may be as rapid as desired, consistent with the need to achieve the indicated desired other process conditions. Pulling speeds for this melt zone **29** may range up to about **10** mm/min., though smaller and larger upper range values may be employed, if desired, as those skilled in the art will appreciate, depending on equipment, process considerations, rod being processed, and the like.

Silicon monocrystalline rods produced by the process of the present invention typically exhibit ρ-breaks in the rod center in a range of from about **20** to **40** percent.

Product monocrystalline rods with closely bounded, drastic fluctuations in resistance radially measured can be conventionally sliced into wafers which are suitable for usage in thyristors of the type which may be ignited in overhead fashion.

Preferably, such product rods are tempered in a separate step, preferably in a separate apparatus (conventional) while being maintained in a solid state at a temperature approaching the melting point of the rod semiconductor material in an inert shield gas atmosphere (e.g. hydrogen, argon, or the like), or in air, to improve their crystalline quality. For example, in the case of silicon rods, such a tempering can be carried out at temperatures in a range of from about **1,300°** to **1,400°C** for a time of at least about five hours, in, for instance a silicon tube, or the like, and the desired wide break in resistance in the center region of such rods so tempered is characteristically substantially retained. A narrow break in resistance is characteristically levelled out in rods during such a tempering.

In one preferred aspect the present invention is directed to a process for preparing an oriented semiconductor monocrystalline rod having a specific resistance which drops towards the center thereof and to aa rod so prepared. In this aspect, one uses the steps of simultaneously and continuously:

A. positioning generally vertically a generally uniformly cross-sectionally circular starting rod comprised of polycrystalline, semi-conductor material in an inert gaseous atmosphere with the bottom end portion of said starting rod being in contact with a seed crystal therefor,

B. positioning a zone of heat annularly about said starting rod said zone of heat being adopted to substantially uniformly heat the portion of said starting rod within said zone of heat to an extent sufficient to uniformly and radially symmetrically melt such portion and to induce conversion of said semi-conductor material from such polycrystalline form to a substantially monocrystalline form upon resolidification of such so melted portion into a resolidified rod said zone of heat initially being adjacent said bottom end portion, said resolidified rod being likewise generally uniformly cross-sectionally circular,

C. moving said zone of heat vertically axially upwardly relative to said starting rod at a substantially uniform rate of at least about **3.5** mm/min. and thereby causing said so melted portion to move similarly upwardly through said starting rod in such uniform and radially symmetrical manner,

D. substantially coaxially revolving said starting rod and said resolidified rod such that said starting rod below said so melted portion revolves at a rate of from about **5** to **100** r.p.m. while said resolidified rod above said so melted portion revolves at a rate of from about **0** to **50** r.p.m.,

E. said positionings, said movings, and said revolving cooperating to cause:

1. the ratio of the diameter of said starting rod to said recrystallized rod to be at least about **1:1**, and

2. the profile of the interface between said so melted portion and said resolidified portion therebeneath to extend transversely across said resolidified rod radially symmetrically, and concavely, relative to the upper end of said rod, with the apex of said interface being at the axis of said resolidified rod.

In such preferred aspect the axial displacement of said semi-conductor material is not more than about **10** percent of the diameter of said recrystallized rod. For example, in the case of a starting silicon rod diameter of about **50** mm, this means an axial displacement of less than about **5** mm, and preferably less than about **4** mm in the case of starting silicon rod diameters of from about **35** to **45** mm. The deviation from the (**111**)-orientation is most preferably under about **1.5°** for silicon rods.

In such preferred aspect, the ratio of the axial length (or height) of said so melted portion relative to the diameter of said recrystallized rod said moving ranges from about **1:1** to **0.5:1.** For example, in the case of a monocrystalline silicon rod diameter of about **30** mm, one preferably selects a molten zone height of about **25** mm, and, for another example, in the case of a rod diameter of about **45** mm, one preferably selects a molten zone height of about **26** mm, and, for yet another example, with a rod diameter of about **70** mm, one preferably selects a molten zone height of from about **28** to **30** mm.

EMBODIMENT

The present invention is further illustrated by reference to the following Example. Those skilled in the art wll appreciate that other and further embodiments are obvious and within the spirit and scope of this invention from the teachings of this present Example taken with the accompanying specification and drawings.

EXAMPLE

Using apparatus of the type shown in FIG. **5**, a preformed, doped polycrystalline silicon rod having a diameter of about **45** mm is mounted vertically between mountings **27** and **28.** A seed crystal contacts the bottom end of the rod. The vessel **21** is purged and charged with hydrogen gas of **99.999** weight percent purity to a pressure of about **100** mm Hg. Initially, the induction coil **30** annularly surrounds the bottom end region of the rod concentrically and radially symmetrically. The coil **30** is energized and the temperature transversely across and within the region of the coil **30** is adjusted so that the temperature of the molten or melt zone **29** therewithin is maintained uniformly. The coil **30** is moved upwardly axially relative to the rod from the bottom portion of the rod at a uniform rate of about **5.5.** mm/min. Simultaneously, the bottom end of the rod in mounting **28** is rotated clockwise (when viewed from above) by shaft **25** at a uniform rate of about **20** r.p.m. while the top end of the rod in mounting **24** is rotated likewise clockwise by shaft **24** at a uniform rate of about **5** r.p.m. As the melt zone **29** moves upwards, the molten rod material solidifies substantially in a monocrystalline form, and the diameter of this so solidified, monocrystalline rod is found to be about **35** mm. A constantly concavely curved boundary area is produced at the solid-fluid phase boundary in the rod to which a (**111**)-tangent can be applied only in the center of the rod. The axial displacement of the diameter of the semi-conductor monocrystalline rod is about **8** percent.

The resulting product rod is removed from vessel **21,** placed in a silicon tube in an air shield gas atmosphere, and tempered in a solid state at a temperature ranging from about **1,325°** to **1,375°** C for about five hours. The crystalline structure of the tempered rod is found to be improved and the desired break in ρ valves near the rod center is substantially maintained after this tempering.

The product silicon rod produced exhibits a specific resistance ρ break in the center of the rod of about **30** percent which is closely bounded. When sliced into wafers, the wafers are found to be useful in thyristers which can be ignited in overhead fashion.

We claim:

1. In a method for the production of a (**111**)-oriented semiconductor monocrystalline rod having a specific resistance which decreases toward the center of said rod whereby a floating melt zone is positioned to annularly encompass a (**111**)-oriented semiconductor starting doped rod and said melt zone is axially moved along said starting rod which is held perpendicularly at both its ends, proceeding from a (**111**)-oriented seed crystal in contact with one end of such starting rod, the improvement which comprises;

adjusting the axis displacement of such starting rod in respect to the axis of the resolidified semiconductor crystal rod being produced from the passage of such melt zone so that such displacement is smaller than **10** percent of the diameter of the semiconductor crystal rod being produced;

axially moving said melt zone at a speed of at least 3.5 mm/min.; and

maintaining a ratio between the diameters of said starting rod to said resolidified rod greater than **1:1.**

2. The process as claimd in claim **1,** characterised in that a drawing speed of preferably about **5.5** mm/min is set.

3. A process for preparing an oriented semiconductor monocrystalline rod having a specific resistance which drops towards the center thereof comprisinng the steps of simultaneously and continuously

A. positioning generally vertically a generally uniformly cross-sectionally circular starting rod comprised of polycrystalline, semi-conductor material in an inert gaseous atmosphere with the bottom end portion of said starting rod being in contact with a seed crystal therefor,

B. positioning a zone of heat annularly about said starting rod said zone of heat being adopted to substantially uniformly heat the portion of said starting rod within said zone of heat to an extent sufficient to uniformly and radially symmetrically melt such portion and to induce conversion of said semiconductor material from such polycrystalline form to a substantially monocrystalline form upon resolidification of such so melted portion into a resolidified rod, said zone of heat initially being adjacent said bottom end portion, said resolidified rod being likewise generally uniformly cross-sectionally circular,

C. moving said zone of heat vertically axially upwardly relative to said starting rod at a substantially uniform rate of at least about **3.5** mm/min. and thereby causing said so melted portion to move similarly upwardly through said starting rod in such uniform and radially symmetrical manner,

D. substantially coaxially revolving said starting rod and said resolidified rod such that said starting rod below said so melted portion revolves at a rate of from about **5** to **100** r.p.m. while said resolidified rod above said so melted portion revolves at a rate of from about **0** to **50** r.p.m.,

E. said positionings, said moving, and said revolving cooperating to cause:

1. the ratio of the diameter of said starting rod to said recrystallized rod to be at least about **1:1,** and

2. the profile of the interface between said so melted portion and said resolidified portion therebeneath to extend transversely across said resolidified rod radially symmetrically, and concavely, relative to the upper end of said rod, with the apex of said interface being at the axis of said resolidified rod.

4. An oriented semi-conductor monocrystalline rod having a specific resistance which drops towards the center of the rod, said rod being produced by the process of claim **3.**

5. The process of claim **3** wherein the axial displacement of said semi-conductor material is not more than about **10** percent of the diameter of said recrystallized rod.

6. The process of claim **3** wherein said moving is accomplished at a substantially uniform rate of from about **3.5** to **10** mm/min.

7. The process of claim **3** wherein said moving is accomplished at a substantially uniform rate of about **5.5** mm/min.

8. The process of claim **3** wherein, in said revolving, said starting rod revolves at a rate of about **20** r.p.m. and said resolidified rod revolves at a rate of about **5** r.p.m.

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