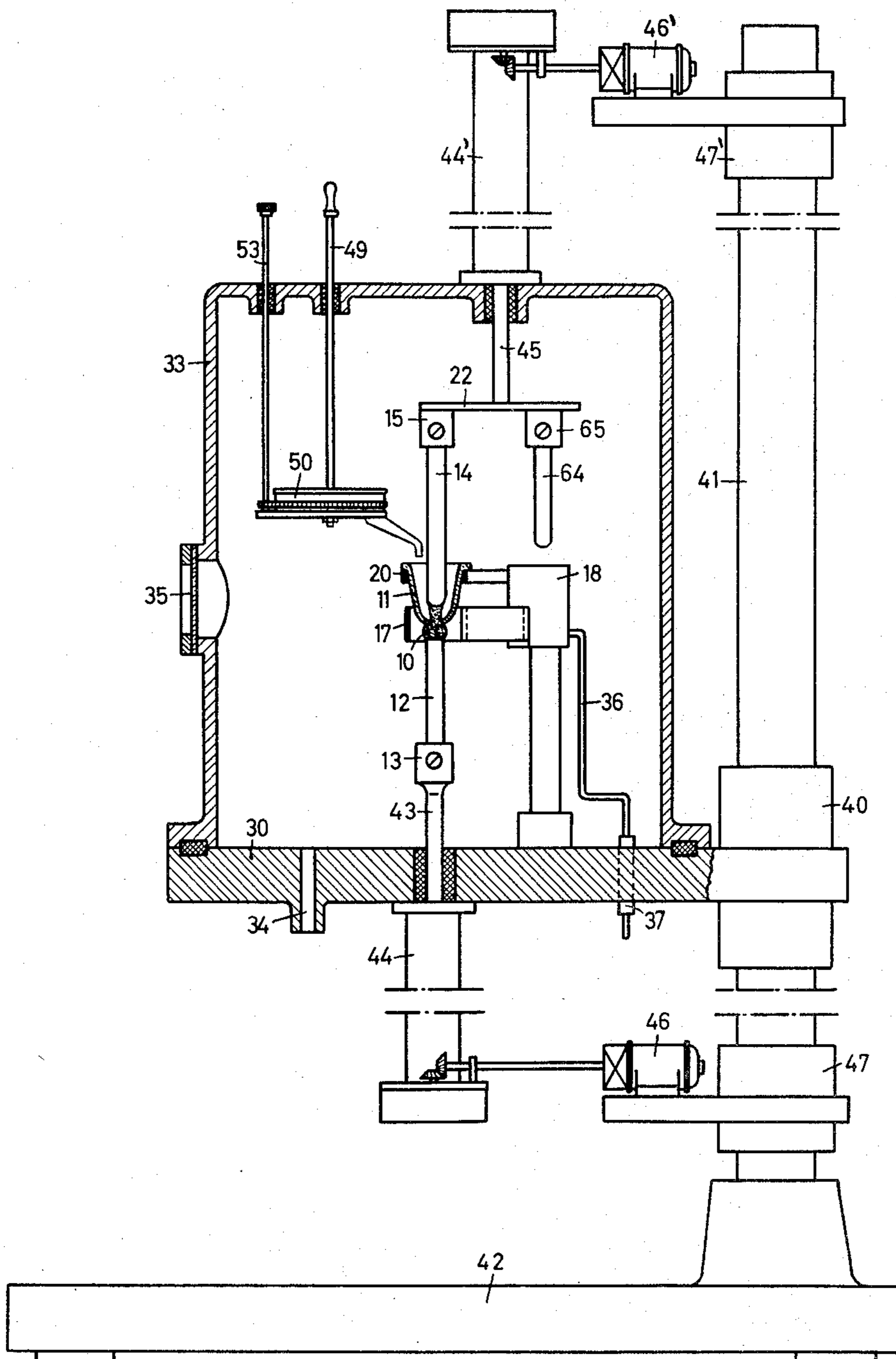


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METHOD FOR PREPARING ROD-SHAPED, CRYSTALLINE  
SEMICONDUCTOR BODIES  
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**METHOD FOR PREPARING ROD-SHAPED, CRYSTALLINE SEMICONDUCTOR BODIES**

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9 Claims. (Cl. 148—1.5)

The present invention relates to the preparation of rod-shaped, crystalline semiconductor bodies, and is a continuation-in-part of the co-pending joint application Serial No. 489,177, filed February 18, 1955, entitled "Apparatus for Preparing Rod-Shaped, Crystalline Bodies, Particularly Semiconductor Bodies."

For certain electrotechnical purposes, monocrystalline semiconductors are required that comprise a series of zones having different conductivity characteristics, for example p-n-p or n-p-n crystals, which may be used as transistors. Other types are indicated below. Such crystals consist of either an elementary base material, such as germanium or silicon, or of a semiconducting compound such as  $AmBv$  compounds of elements in the third and fifth groups of the periodic system, or  $AmBv$  compounds of elements in the second and sixth groups of the periodic system. The different conductivity characteristics of individual parts of the crystal depend upon the content of various addition agents or substitutional impurities acting either as excess-electron producers (donor substances), causing n-conductance, or as defect-electron producers (acceptor substances), causing p-conductance, depending upon which of the two addition agents is present in larger amounts in the base material.

Generally, monocrystalline structures of the aforementioned materials are prepared by pulling the crystal from a melt of the desired material. In order to pull a p-n-p monocrystal from a melt, such as p-conductive germanium, an addition agent or substitutional impurity must be added twice to the melt during the pulling process. In the past, after having pulled, for example, a p-zone from molten, p-conductive germanium, a donor substance such as antimony was added to the melt in such an amount that it would exceed the acceptor substance in the solid product and, after having pulled an n-zone in this manner, an acceptor substance such as gallium was added in a correspondingly higher amount, in order to obtain a p-zone upon further pulling from the melt. Inasmuch as the amounts of addition agents, and therewith the conductivities, increase progressively upon a repeated reversal in this manner of the conductivity characteristics, the number of such reversals is obviously limited.

It is the principal object of the present invention to permit melt-pulling of a semiconductor crystal having a succession of zones of different conductivity characteristics whereby, instead of a progressive increase in the conductivity, the conductivity of the individual zones is successively altered at will.

It is another object of the invention to employ, in conjunction with the making of the afore-described semiconductor crystals, substantially reduced amounts of molten material, preferably amounts that are smaller than the resulting crystalline body and, therefore, permit the use of a very small crucible and the addition of new melting material during the pulling process.

It is a further object to change the conductivity characteristics of a melting crystal at a relatively small material expenditure and as often as desired.

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It is a final object of the invention to prepare new semiconductors having an unlimited succession of zones of differing conductivity characteristics.

Other objects and features of this invention will appear more fully and clearly from the following description, when considered in conjunction with the appended drawing, illustrating a preferred embodiment of an apparatus for making these new semiconductors.

The present invention is based on the finding that, after preparing one zone of a semiconductor, an increase in the conductivity of the next zone can be avoided by again reducing the amount of addition agents in the liquid melt. For this purpose, it is necessary to first reduce as much as possible the amount of liquid melt remaining after the making or pulling of the preceding zone. According to this invention, subsequent to the pulling of a melting rod zone with lattice defections because of the presence of an addition agent, part of the liquid melt remaining in the crucible is removed prior to the addition of fresh melting material. This can be done, for example, by means of pulling an auxiliary melting rod. Inasmuch as this auxiliary melting rod does not need to be monocrystalline, the speed of pulling can be as high as possible in accord with the surface tension of the melt. A relatively high distribution coefficient may be thereby obtained, particularly if the ordinarily employed rotation of the melting rod is avoided, and the larger part of the addition agent may be removed from the melt. By adding new raw material of suitable composition, the addition agent contained in the residual drop of liquid material is greatly diluted and a new zone of monocrystalline melting rod may be pulled which has an even lower conductivity than the preceding zone.

In this manner, any change in the conductivity characteristics of the various zones of a melting crystal can be attained at relatively small material expenditures, and monocrystalline melting rods having an unlimited number of zones of different conductivity can be prepared. Various auxiliary melting rods may be provided for alternately emptying the crucible, by pulling the liquid out of the crucible, and each of the auxiliary rods may be reserved for removal of one type of additional material.

The herein-claimed method is advantageously carried out in such a manner that the desired monocrystalline rod is pulled in a downward direction while new material is added from above. The new material can be in granular, particularly fine-granular, form or in the shape of a sintered or melting rod. Moreover, a plurality of supply rods comprising different amounts of one additional material may be used alternately in the making of one zone of the monocrystalline body.

Referring more particularly to the drawing, there is shown a crucible 11 containing a small amount of the raw material in the liquid state. The crucible has a discharge opening for liquid material at the bottom. Shown underneath this opening is a previously pulled section 12 of a monocrystalline rod whose lower end is fastened to the clamping support 13. This clamping support is movable in the direction of the axis of the melting rod so that, by means of the clamping support, the melting rod may be gradually moved downward. As a result thereof, a drop 10 of the material in question, held between the upper part of the melting rod 12 and the crucible 11, gradually and progressively cools and solidifies from below so that the melting rod grows in an upward direction. The pulling motion is transmitted to the shaft 43 from a lower drive 44, actuated by two motors 46 (of which only one is shown). Moreover, aside from the axial movement, and independently therefrom, the drive 44 is capable of also transmitting a rotational movement to the shaft 43. The lower drive 44 is fastened to a base plate 30, made from steel, through which the shaft 43

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is passed, mounted in an air-tight sleeve. Likewise fastened to the base plate is the stand 18 with a lateral support 20 for holding the crucible 11. Annular heating means 17, also fastened to the stand 18, surround the lower section of the crucible. Leads 36, passing through air-tight insulating sleeves 37, inserted into the base plate 30, connect the heating means with an adjustable heating transformer (not shown).

The entire arrangement is covered by a steel dome 33 fitting air-tight onto the base plate 30 and provided with a show glass 35. The base plate 30 has a nipple 34 to connect a vacuum pump or a container of inert gas to the device. The base plate is held by an adjustment bushing 40, by means of which the entire device is displaceable along a support column 41 extending from a pedestal 42.

The crucible 11 is charged with base material in form of a rod or ingot 14 suspended from a clamping support 15. Moreover, an auxiliary ingot 64, suspended from a clamping support 65, is mounted above the crucible 11. The clamping supports 15 and 65 are fastened to a turntable 22, the shaft 45 of which passes in an air-tight manner through the top of the dome 33. By means of two motors 46' (only one of which is shown), the drive 44', connected with the shaft 45, can be moved axially and, independently therefrom, be turned in such a manner that, according to the requirements, either the auxiliary ingot or the supply ingot is exactly vertically above the crucible when turned into operative position. If the use of a plurality of auxiliary ingots and supply ingots is desired, they may be also suspended from the turntable 22.

In order to furnish addition agents to the melt, a device 50 is provided which is fastened to a rod 49 passing in an air-tight manner through the top of the dome 33. As has been more fully described in the afore-mentioned co-pending application, addition agents, in form of granules or pills, deposited therein, can be added to the melt in predetermined amounts according to a desired addition schedule. The required rotation over a small arc of the device at established time intervals is accomplished by means of the rod 53, either by hand or by means of a suitable coupling drive, or an electric drive operating in synchronism with the crystal pulling process.

The method of operation is as follows. As soon as the upper extremity of the growing monocrystalline rod 12 has been made into, say, a p-zone, the supply ingot 14 is lifted out of the crucible and replaced by the auxiliary ingot 64 until the lower end thereof just touches the liquid melt. Upon a relatively quick removal of the auxiliary ingot, the melt contained in crucible 11 is withdrawn, clinging to the ingot, and solidifying in contact therewith. Only a substantially small amount of melt, such as the drop 10, remains in the crucible. Now, if the supply ingot 14, which does not contain any addition agent capable of changing the electrical characteristics, is moved into contact with the crucible, and an amount of material of the supply ingot is liquefied which is, for example, nine times the amount of the drop 10, the concentration of addition agent in the melt has been reduced to one tenth of the previous concentration. Consequently, the melt also has a reduced conductivity and can now be supplemented with an addition agent delivered from device 50 for pulling, say, an n-zone. The amount of this addition agent can be readily limited in such a manner that the conductivity of the resulting n-zone does not exceed the conductivity of the previously made p-zone. The remaining melt, supplemented with the addition agent, can be removed from the crucible in the afore-described manner by means of the same or another auxiliary ingot, in order to supplement a subsequent quantity in the opposite sense. The alternate supplementation with addition agents can be carried out for an unlimited number of times. In the alternative, a plurality of successive zones may be prepared that have the same conductivity characteristic but differ in their conductivity

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rate. Moreover, zones of the same or different conductivity characteristics in which, therefore, either a donor or acceptor agent prevails, may be interspersed with other zones containing a balance of such opposite types of addition agents. The desired sequence of zones is determined by the order of charging the individual compartments of addition device 50 with the respective agents.

The described crystal pulling method is particularly useful for the making of various transistors and "Hall" rectifiers having series of n<sub>1</sub>-n<sub>2</sub>-p or p<sub>1</sub>-p<sub>2</sub>-n zones, respectively.

Suitable principal materials are, generally speaking, the elements germanium and silicon as well as compounds of elements in the third and fifth groups of the periodic system, such as AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InSb, InAs, of which germanium (M. P. 958° C.), silicon (M. P. 1420° C.) and aluminum antimonide (M. P. 1050° C.) are preferred. While germanium and silicon can be handled in vacuo or in an inert gas, aluminum antimonide requires a rare gas, such as an atmosphere of argon or helium. Purest graphite is used as crucible material when working with germanium, sintered corundum (Al<sub>2</sub>O<sub>3</sub>) when working with aluminum antimonide (AlSb) and quartz (SiO<sub>2</sub>) when working with silicon. In order to prepare from germanium or silicon monocrystalline bodies having n-conductive and p-conductive zones respectively, elements of the fifth group of the periodic system, such as P, As, Sb and Bi, are added to produce n-conductive zones, and elements of the third group, such as B, Al, Ga and In, to produce p-conductive zones. For the preparation of zone-different monocrystalline bodies from compounds of elements in the third and fifth groups of the periodic system as the principal material, elements of the sixth group, such as S, Se and Te, are suitable as addition material to produce n-zones, and elements of the second group, such as Zn, Cd and Hg, to produce p-zones.

As a typical example, the pulling of a zone-different monocrystalline body of germanium is described:

A graphite crucible having a capacity of about 2 ccm. is charged with p-conductive germanium, containing a small amount from 0.001 to 0.0001 percent of gallium so as to have a specific resistance of about 0.12 ohm cm. As the next step, a seed crystal in form of a previously prepared, short germanium rod having a cross-sectional area of about 1 cm.<sup>2</sup> is moved from below against the crucible opening. Then the crucible is heated in order to melt the charge. The heating temperature is regulated to the melting point of germanium and is kept constant at 958°+0.1° C. The crystal is pulled, as previously described, at a speed of about 0.3 mm./min. while simultaneously rotating at 250 to 500 revolutions/min. After about five minutes, a p-conductive zone 1.5 mm. in length has been added to the monocrystalline body. Because of the slow speed of the pull, the distribution coefficient *k* of gallium in germanium is 0.1, which results in a specific resistance of 1 ohm cm. for the p-zone pulled in this manner. As the next step, a germanium rod of highest possible resistance (auxiliary ingot 64) is dipped from above into the remaining melt in order to remove the melt from the crucible. This is done at a relatively high pulling speed (about 6 mm./min.) and without rotating the ingot. According to Slichter and Kolb (Phys. Rev. 90, No. 3, 1953, page 987), the distribution coefficient *k* for gallium in germanium is about 0.5 under these conditions. Aside from a small drop inside or below the crucible opening, the volume of which is about 0.15 ccm., the entire melt is removed from the crucible within a few minutes. By means of a supply ingot 14, consisting of germanium containing a small amount of, say, arsenic, the crucible is recharged with melt. The amount of this addition material, producing n-junctions, may be in the range from 0.00001 to 0.0002 percent and is adjusted in

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such a manner that the total amount of As in 1.5 ccm. of the Ge-melt is only slightly higher than the amount of Ga in the 0.15 ccm. of the remaining drop. Thus, the entire melt, including the remaining drop, is adjusted to n-conductance. The zone to be produced therefrom is to be only about 30  $\mu$  in length which, at a pulling-speed of 0.3 mm./min., is accomplished after about six seconds of pull. This zone has a resistance about five times as high as the previous zone; thus, in the instant case, a resistance of about 5 ohm cm. The next zone is prepared in the same manner. For transistors, this zone is to be p-conductive, for "Hall" rectifiers it is to be n-conductive.

In order to produce the former, the crucible is again emptied by rapidly (6 mm./min.) withdrawing the ingot 14 and charging the crucible with p-conductive melt by inserting the ingot 64. The required p-zone of several millimeters in length is pulled at a speed of 0.3 mm./sec. and the specific resistance thereof is again about 1 ohm cm. Upon repeating the foregoing process, an optional number of p-n-p transistors with increased basic resistance can be combined in one rod.

In order to produce so-called "Hall" rectifiers, after pulling of a narrow n-zone, a second n-zone of increased conductivity is prepared by charging the crucible with melt from another auxiliary ingot made of germanium having a specific resistance which is lower than that of the n-conductive ingot 14. Moreover, it is also possible to increase the, say, arsenic content of the melt by adding, after the second pulling step, a small amount of germanium-arsenic alloy to the melt in form of a pill delivered by the device 50. In this manner, a p-n<sub>1</sub>-n<sub>2</sub> sequence is obtained wherein the specific resistance of the n<sub>1</sub>-zone is higher than that of the n<sub>2</sub>-zone.

Series such as the series n-p-n or n-p<sub>1</sub>-p<sub>2</sub> can be produced in the same manner.

The advantage of this method as against the prior pulling method requiring reversal of the conductivity characteristics of the entire content of a relatively large crucible consists in the fact that, because of a volumetric ratio of, say, 1:10, between the residual drop and the entire melt, the amount of additional material going into the melt can be reduced, resulting in an increase of the specific resistance. However, the distribution coefficient of the additional materials in the melt must be high because of the danger that otherwise the residual drop may contain substantially all of the additional material originally contained in the melt.

I claim:

1. A method of preparing a rod-shaped, plural-zoned monocrystalline semiconductor body having at least one zone containing a substitutional impurity substance conferring a conductivity type characteristic different from an adjacent zone, the substitutional impurity substance of said one zone being selected from the group consisting of p and n conductivity type determining impurities, which comprises the steps of melting in a crucible an amount of material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body and consists of a mixture of a semiconductor and an amount of said impurity substance causing one of said types of conductivity, pulling a zone of said crystalline body from the melt, removing remaining melt from the crucible excepting a residual drop in contact with said crystalline body, charging the crucible with a similarly limited amount of semiconductor material having a conductivity type characteristic differing from that of said pulled zone, heating said last-named mixture to form a melt, and pulling another zone of said crystalline body from the melt.

2. Method of preparing rod-shaped, monocrystalline semiconductor bodies having zones containing substitutional impurity substances so as to possess different conductivity characteristics, which comprises the steps of

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charging a crucible with an amount of material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body and consists of the mixture of a semiconductor and an amount of an acceptor substance causing p-conductance, heating said mixture to form a melt, pulling a zone of said crystalline body from the melt, removing remaining melt from the crucible excepting a residual drop in contact with said crystalline body, charging the crucible with a similar amount of material consisting of a mixture of said semi-conductor and an amount of a donor substance causing n-conductance and at least counterbalancing any p-conductance caused by acceptor substance contained in said residual drop, heating said last-named mixture to form a melt, and pulling another zone of said crystalline body from the melt.

3. A method of preparing a rod-shaped, plural-zoned monocrystalline semiconductor body having at least one zone containing a substitutional impurity substance conferring a conductivity characteristic different from an adjacent zone, the substitutional impurity substance of said one zone being selected from the group consisting of p and n conductivity type determining impurities, which comprises the steps of melting in a crucible an amount of material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body and consists of a mixture of a semiconductor and an amount of said impurity substance causing one of said types of conductivity, pulling a zone of said crystalline body from the melt, removing remaining melt from the crucible excepting a residual drop in contact with said crystalline body, by dipping into the melt an auxiliary ingot having substantially the composition of the main constituent of the melt, and heating and pulling the melt out of the crucible, the melt clinging to the auxiliary ingot, charging the crucible with a similarly limited amount of semiconductor material having a conductivity type characteristic differing from that of said pulled zone, heating said last-named mixture to form a melt, and pulling another zone of said crystalline body from the melt.

4. The method of preparing a monocrystalline semiconductor body, the body having adjacent zones differing in conductivity rate or characteristic, by pulling a crystal from a melt, which comprises charging a crucible with an amount of the semiconductor material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body, heating said amount of material to a melt, pulling said crystalline body from the bottom of the melt, removing the melt remaining in the crucible, excepting a residual drop in contact with said crystalline body, by dipping into it an auxiliary ingot, the melt material clinging to the ingot as it is retracted, adding an amount of a second material to that part of the first melt still remaining in the crucible, said second material having a different conductivity rate or characteristic than the first recited semiconductor material, heating the two to form a second melt, and pulling another zone of said crystalline body from the bottom of the second melt.

5. Method of preparing a rod-shaped, plural-zone monocrystalline semiconductor body having at least one zone containing a substitutional impurity substance conferring a conductivity type characteristic different from an adjacent zone, the substitutional impurity substance of said one zone being selected from the group consisting of p and n conductivity type determining impurities, which comprises the steps of charging a crucible with an amount of material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body and consists of the mixture of a semiconductor and an amount of a substitutional impurity substance conferring one of the said types of conductivity, heating said mixture to form a melt, pulling a zone of said crystalline body from the melt,

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removing remaining melt from the crucible excepting a residual drop in contact with said crystalline body, charging the crucible with a similarly limited amount of material consisting of a mixture of said semiconductor and an amount of a substitutional impurity substance at least counterbalancing any conductivity type characteristic caused by substitutional impurity substance contained in said residual drop, heating said last-named mixture to form a melt, and pulling another zone of said crystalline body from the melt.

6. Method of preparing a rod-shaped, plural-zoned monocrystalline semiconductor body having at least one zone containing a substitutional impurity substance conferring a conductivity characteristic different from an adjacent zone, the substitutional impurity substance of said one zone being selected from the group consisting of p and n conductivity type determining impurities, which comprises the steps of charging a crucible with an amount of material from which the crystal is to be pulled that represents not more than a fraction of the material making up the finished crystalline body and consists of the mixture of a semiconductor and an amount of a substitutional impurity substance conferring one of the said types of conductivity, heating said mixture to form a melt, pulling a zone of said crystalline body from the melt, removing remaining melt from the crucible excepting a residual drop in contact with said crystalline body, by dipping into the melt an auxiliary ingot having substantially the composition of the main constituent of the melt, and heating and pulling the melt out of the crucible, the melt clinging to the auxiliary ingot, charging the crucible with a similarly limited amount of material consisting of

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a mixture of said semiconductor and an amount of a substitutional impurity substance at least counterbalancing any conductivity type characteristic caused by substitutional impurity substance contained in said residual drop, heating said last-named mixture to form a melt, and pulling another zone of said crystalline body from the melt.

7. The method of preparing a monocrystalline germanium semiconductor crystal comprising pulling a zone of p-conductive germanium, in which the acceptor substance is gallium, from a melt thereof in a crucible by means of a seed crystal of germanium, dipping a germanium rod into the melt to remove substantially all of the melt except for a residual drop, melting in the crucible germanium containing at least sufficient arsenic to counteract the acceptor substance in the residual drop, and pulling a zone of conductivity characteristic, differing from the first zone, from the melt.

8. The method defined in claim 2 in which the acceptor substance is taken from the elements of the third group of the periodic system.

9. The method defined in claim 2 in which the semiconductor material is taken from the group consisting of germanium, silicon, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InSb and InAs.

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