June 29, 1965 MASAMI TOMONO ETAL 3,192,082

PROCESS FOR THE PRODUCTION OF npn OR pnp JUNCTION

Filed Oct. 23, 1962

Fig. 1.

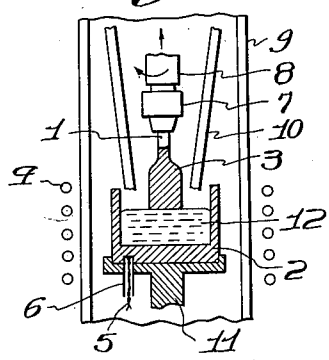


Fig. 2.

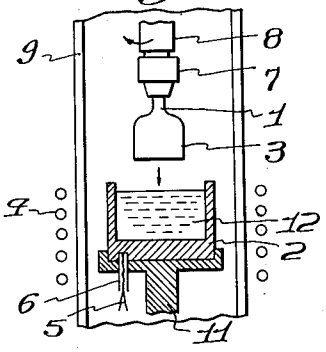


Fig. 3.

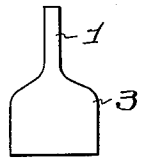


Fig. 4.

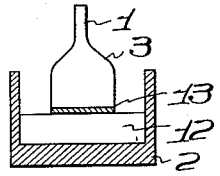


Fig. 5.

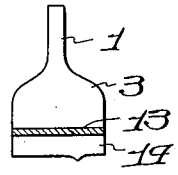


Fig. 6.

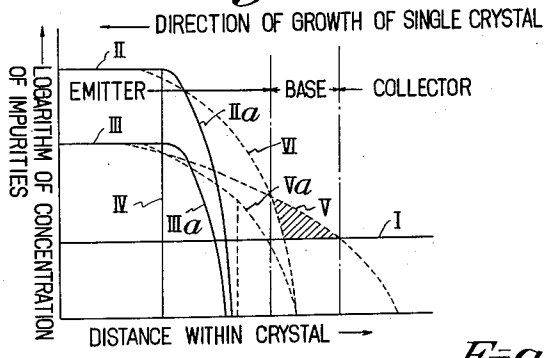
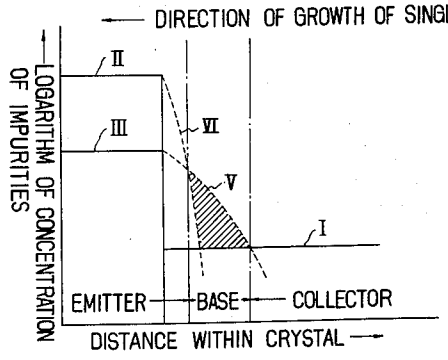


Fig. 7.



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3,192,082
PROCESS FOR THE PRODUCTION OF npn OR pnp JUNCTION

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1 Claim. (Cl. 148—172)

This application is a continuation-in-part of application Serial No. 859,222, filed December 14, 1959 now abandoned.

This invention relates to a process for the production of npn junctions or pnp junctions.

A principal object of this invention is to provide a process for the production of single crystals capable of making transistors having regular and uniform electrical characteristics without depending on the position relative to the axis of the single crystal.

Another object of this invention is to provide a process for the production of single crystals capable of making transistors with considerably high yield and making transistors with high cut-off frequency.

The above-mentioned objects, other objects, details, and advantages of this invention will be apparent from a consideration of the following detailed description taken in conjunction with the accompanying drawings, in which the same or equivalent parts are designated by the same numerals and in which:

FIG. 1 and FIG. 2 are sectional diagrams, in elevational view, of an apparatus for the production of single crystals for transistor, particularly suited for practicing the method of this invention;

FIG. 3 shows, in sectional elevation, a semiconductor crystalline ingot, a stock material used in carrying out the method of this invention;

FIG. 4 is an elevational view for the explanation of the formation of the npn or pnp structure when the present method is carried out;

FIG. 5 is an elevational view, in section, with a part cut away, of a semiconductor monocrystalline ingot having npn or pnp structure, made by the present method;

FIG. 6 is a graphical representation showing the distributions of the concentrations of the impurities within a single crystal of the grown diffused type made by a conventional method; and

FIG. 7 is a graph showing the equivalent curves for a single crystal made by utilizing the present method.

The apparatus such as that indicated in FIG. 1 has been used previously for the production of single crystals to be used for grown diffused junction type transistors.

Referring to FIG. 1, numeral **1** designates a single crystal seed. The condition wherein a semiconductor single crystal **3** is being pulled up from the molten material within a suitable crucible **2** is also illustrated in FIG. 1. The single crystal seed **1** is held by a chuck **7**, which pulls up the single crystal **3** as it is rotated by a crystal pulling shaft **8**. The crucible **2** rests on a quartz table **11** and is heated by a high-frequency coil **4** wound concentrically thereabout, and concentrically about a vertical furnace tube **9** made of transparent quartz, through which an inert gas is made to flow. A thermocouple **5** within a guard tube **6** is inserted into the bottom of the crucible **2**. Quartz tubes **10** are directed toward the crucible **2** for the purpose of "doping" or adding impurities to the molten semiconductor during the pulling up of the single crystal.

The production of a single crystal of the grown diffused type for transistors by means of such an apparatus as described above will now be described with the aid of an

example for the particular case of germanium. A single-crystal seed **1** of germanium is immersed in molten germanium **12** to which indium has been added to that the concentration of indium in it will be about $1\times10^{18}/cm.^3$ and its specific resistance will be of the order of 1Ω cm. To begin with, a single crystal **3** is pulled up and, after a certain period of this process, the velocity of pulling the single crystal is decreased. Then, under this condition, an acceptor impurity (for example: gallium) and a donor impurity (for example: antimony) in comparatively large quantities are added simultaneously by dropping into said "melt" or molten liquid (for example, the impurity concentrations of gallium and antimony in the molten germanium are 4×10^{18} and 1×10^{19} per $cm.^3$, respectively), and the process of drawing up the single crystal is continued for a predetermined period of time to form the single crystal. For the acceptor impurity to be used in this case, a substance having a high value of segregation constant and low value of diffusion constant with respect to germanium is selected; and for the donor impurity a substance having a low segregation constant and high diffusion constant with respect to germanium is selected. It is necessary to accurately determine and control the quantities of the impurities added so that, in the single crystal created after the doping, a quantity of the acceptor impurity which is larger than that of the donor impurity is contained, and the crystal is a p-type crystal, and so that, the quantity of the donor impurity in the p-type single crystal drawn up thereafter is substantially larger than that of the acceptor impurity in the p-type single crystal drawn up initially. If the crystal is made in this manner, although the single crystal grown after the impurities have been dropped in is of the p-type, the donor impurity (for example: antimony) contained in said single crystal infiltrates into the single-crystal region which has grown prior to the addition of said impurities owing to the diffusion within the solid and cancels the p-type conductivity caused by the acceptor impurity (for example: indium) existing beforehand in said region, thus forming a thin layer having n-type conductivity. In this case, the region of the p-type single crystal which was grown initially shall be called the "collector region"; the region of the p-type single crystal which was grown finally and contains a large quantity of the acceptor impurity shall be called the "emitter region"; and the n-type thin layer formed by the diffusion of the impurities from the emitter region towards the collector region shall be called the "base region."

The distribution of concentration of the impurities within the germanium with respect to the distance within the crystal of a single crystal obtained in this manner is as shown in FIG. 6, in which the abscissa represents the distance within the crystal, and the ordinate represents the concentration of the impurity, both being given suitable scales, and the direction of growth of the single crystal is indicated by the arrow.

Curve I represents the concentration distribution of a p-type impurity (indium) existing from the beginning and indicates a substantially uniform distribution within the crystal. Let it be assumed now that a comparatively large quantity of gallium, as acceptor impurity, and antimony, as a donor impurity, are added simultaneously at a position corresponding to A. The growth of the single crystal continuing to progress meanwhile, the added acceptor and donor impurities dissolve into the molten germanium and, as a result of agitation and diffusion, reach the growth interface. As this movement requires time, the concentration of the impurities within the molten germanium directly below the growth interface of the crystal progressively increases with time, and the single crystal which contains the impurities of a quantity corresponding

thereto is made to grow. Consequently, in the portion to the left of the point A in FIG. 6, the impurity concentrations of the gallium and antimony rise gradually as indicated, respectively, by full lines II*a*, III*a* of the drawing; and in the portion to the left of the vertical lines IV, wherein the condition is one of substantially uniform distribution of these impurities within the molten germanium, the concentration distribution curves of the impurities within the single crystal, corresponding to the total quantity of the added impurities, become level as indicated by II and III.

The above concentration distributions are hypothetical in that the diffusion of impurities in the solid is not considered. In the actual case, however, because of the effect of high temperature immediately below the melting point which prevails during the drawing up of the single crystal, diffusion of the impurities within the single crystal which has been developed does not take place, and the impurities diffuse from the emitter region towards the collector region.

Within the germanium during this diffusion, the diffusion of the antimony is considerably greater than that of the gallium. Accordingly, in FIG. 6, the concentrations of the antimony and gallium are distributed as indicated, respectively, by V or V*a* and VI.

By cutting out a square cross-section bar of a size of the order of approximately 0.4 mm. x 0.4 mm. x 3 mm., longitudinally parallel to the direction of growth of the single crystal, from the pnp junction region of a single crystal made in the above manner, letting the emitter region, base region, and collector region of the single crystal be, respectively, the emitter, base, and collector, and attaching suitable electrodes to said parts, a pnp-type transistor can be made. However, the production of grown diffused type transistors by the above-described, conventional method entails the following disadvantages.

The first disadvantage is in that, because the impurities which have been dropped in the above-described manner into the crucible dissolve in the peripheral portion thereof and, under agitation, gradually diffuse toward the central portion of the crystal, and the rise in the impurity concentrations at said central portion lags behind that at the peripheral portion. Therefore, as represented on the graph of FIG. 6, the slopes of the curves II*a* and III*a* do not become equal for the portions at the interior and exterior of the axis of the single crystal.

Consequently, the width of the base domain of then n-type created by the diffusion of the impurities within solid varies depending whether the portion is taken from near to or far from the axis of the single crystal. As a result, a transistor made from this single crystal will have irregular electrical characteristics depending on the position relative to the axis of the single crystal.

The second disadvantage is in that, even when the impurities having such concentration distributions as described above diffuse, if the diffusion time is short, the antimony diffusion curve will be to the left of the gallium diffusion curve VI, as indicated by V*a* of FIG. 6, and a case may occur wherein a base domain is not formed. If the diffusion time is longer than that just mentioned, and the antimony diffusion curve has infiltrated to the right of the gallium diffusion curve VI, as indicated by V, a base domain canceling the p-type conductivity due to indium and having the n-type conductivity with a surplus of antimony is formed at the shaded portion of FIG. 6. Therefore, if an attempt is made to raise the cut-off frequency of the transistor by shortening the diffusion time of the impurities and decreasing the thickness of the base domain, an antimony concentration distribution such as that of curve V*a* of FIG. 6 will develop locally; that is, a region with no pnp junction will develop; the yield of the transistor will be lowered considerably; and the production of a trasistor with high cut-off frequency will be extremely difficult.

In contrast to this conventional method, the process of the present invention can effectively eliminate all the various disadvantages as described above. It will be explained with the aid of the following examples. It is, of course, to be understood that these examples are only illustrative and are not intended to limit the scope of the invention.

Example 1

The first embodiment of this invention relates to the case of germanium. By means of an apparatus such as that illustrated in FIG. 1, a single crystal of the collector region whose specific resistivity is about 1 Ω/cm. is pulled up in the conventional manner with the pulling velocity of approximately 1 millimeter per minute. In this case, the impurity concentration of acceptor impurity (indium) in molten germanium is about $1 \times 10^{18}/cm.^3$. Then, the pulling velocity is lowered to approximately 0.1 millimeters per minute, and such quantities of gallium and antimony that their concentration may be, respectively, about $4 \times 10^{18}/cm.^3$ and $1 \times 10^{19}/cm.^3$ are added into the molten germanium for instance their concentration in the molten germanium are $4 \times 10^{18}/cm.^3$ and $1 \times 10^{19}/cm.^3$ respectively, the furnace temperature being simultaneously raised by approximately 3 to 10 degrees C. 15 to 20 seconds are required to raise the temperature of the molten germanium, and during this time, the crystal should be pulled up approximately 0.03 millimeters and should grow. However, instead of the expected crystal growth, melting of the crystal of about 0.2 to 0.5 millimeters takes place because of the rise in temperature of the molten germanium. During the period from the starting of the doping of the emitter region to the melting of the crystal due to temperature rise of the molten germanium, the added impurities are diffused into and mixed with the molten germanium and assume a substantially uniform distribution. Then, under this condition, the variation of furnace temperature is controlled to be extremely small for about 20–30 seconds so that no further growing or melting of the single crystal takes place, or so that the growth or melting takes place at an extremely small rate. While this condition is maintained, the impurities will diffuse from the molten germanium, through the interface between the solid phase and the liquid phase, into the germanium single crystal. Then, after the elapse of the required time, the furnace temperature is cooled rapidly at a cooling rate of approximately 100 degrees C. per minute, the pulling up of the single crystal is completed at a high velocity, and the emitter region crystal is grown. In this manner a single crystal as illustrated in FIG. 5 is obtained. In the drawing, the numeral **1** designates the seed crystal, **3** designates the collector region of the single crystal, **14** designates the emitter region, and the shaded portion **13** is the n-type base domain produced by the diffusion of antimony from the molten liquid into the collector region.

Example 2

We would now like to give a second example in which the scope of this invention is greatly extended and becomes applicable in wider range. An apparatus as illustrated in FIG. 2 is used to carry out the production of a single crystal.

Referring to FIG. 2, reference numerals **1** through **12**, designate the parts which are same or equivalent, respectively, to the parts similarly designated in FIG. 1. However, in the case of FIG. 2, such quantities of gallium and antimony that their concentration in a molten germanium **12** may be, respectively, about $4 \times 10^{18}/cm.^3$ and $1 \times 10^{19}/cm.^3$ had been added beforehand to said molten germanium **12**, and they have been maintained in a molten state for a period of time required to attain the uniform distribution of gallium and antimony in said molten germanium **12**. Single crystal **3** is a part which is to become the collector region of a transistor and is a crystal which has been prepared beforehand by adding

indium and being made to have a specific resistance of approximately 1Ω cm.

The indium concentration in the collector single crystal is about 4×10^{15}/cm.^{3}.

While the temperature of the furnace is maintained constant, the shaft **8** is slowly lowered as it is rotated until the single-crystal ingot **3** is immersed to a very slight depth in the molten germanium **12**. This condition is then maintained until the thermal equilibrium has been established between the melt **12** and solid **3**, then the temperature of the molten germanium **12** is raised by 3 to 10 degrees C. From 15 to 20 seconds are required for this temperature rise to be completed, during which time, approximately 0.2 to 0.5 millimeters of the crystal **3** is melted. If this condition is maintained at the same temperature for a further 20 to 30 seconds, there will be established a state in which the single crystal **3** is neither growing nor melting, but the germanium single crystal **3** and germanium melt **12** are still existing in mutual contact. This temperature control can be effected by means of an automatic temperature controlling device of very high precision. During this period, principally antimony diffuses from within the molten germanium **12**, through the crystal interface, into the germanium single crystal **3**; cancels the action of the induim existing beforehand in this portion; and causes the conversion into an n-type germanium. The reason for this result is that the constant of diffusion of antimony into germanium is approximately 200 times that of gallium.

The aforesaid state is represented schematically in FIG. 4, wherein, reference numeral **12** designates the molten germanium, and the shaded portion **13** represents the n-type layer produced by the diffusion of antimony from within the molten germanium into the single crystal.

After said diffusion of antimony into the germanium single crystal **3** has been completed, the process is continued by rapidly cooling the furnace at a rate of approximately 100 degrees C. per minute; promptly pulling up the single crystal; and causing the growth of an emitter portion of the crystal. This rapidly grown portion is a p-type single crystal containing a large quantity of gallium. The reason for this result is that the segregation constant of gallium with respect to germanium is approximately 30 times that of antimony. Thus, a germanium single crystal possessing pnp junction as illustrated in FIG. 5 is obtained.

In the fabrication of transistors from pnp junctions obtained by the process as described above of this invention, the following advantages will be gained in comparison with the products of the conventional, grown diffused methods.

An advantage is in that, because molten germanium to which gallium and antimony have been added is prepared, and the impurities within the melt are diffused and mixed uniformly before the emitter region is caused to grow, irregularities of impurity concentrations depending on the position with respect to the center of the single crystal, as in the case of products made by the conventional methods, is totally eliminated. Consequently, the thickness of the n-type layer formed by the diffusion of the antimony is extremely uniform, and the deviations of the electrical characteristics of transistors fabricated from this single crystal are exceptionally small.

The second advantage is in that, because the impurities within the germanium melt are made to diffuse, through the interface of contact between the solid and liquid phases, into the solid germanium having both the germanium melt and solid germanium in a state of thermal equilibrium, it is possible to produce an n-type base region of extreme thinness and uniformity. A hypothetical distribution of impurity concentrations, in which diffusion is not considered, in the vicinity of a base region is indicated in FIG. 7, wherein a stepwise change should occur in moving from the collector side to the emitter side. In this illustration, curve I represents the concentration of indium, which is uniformly distributed from the collector side to a portion of the emitter side; curves II and III represent, respectively, distribution of concentrations of gallium and antimony, which are uniformly distributed on the emitter side; and broken curves VI and V represent, respectively, distribution of concentrations of gallium and antimony diffused from within the melt to the collector side. The shaded portion represents the n-type base domain created by the diffusion of antimony. As may be understood from a study of these curves, in contrast to products of the conventional methods having concentration distributions as illustrated in FIG. 6, an extremely thin base domain (in this case, an n-type germanium layer produced by the diffusion of antimony) is obtained regardless of how short the diffusion time is.

Yet, another advantage is in that, because the crystal is remelted before the diffusion of the impurities, said diffusion is made to take place from an extremely fresh interface between the solid and liquid phases, and, moreover, said interface is maintained at the melting point of germanium and is an isothermic surface. Accordingly, said diffusion takes place with extreme uniformity in the direction perpendicular to the interface. As a result, it is possible to form a base region having a considerably fine, sharp, and uniform thickness.

Further advantages of the process of the present invention may best be described by the following comparison thereof with conventional processes.

In the conventional process utilizing apparatus as illustrated in FIG. 1, a single crystal **3** of relatively high specific resistance is first pulled up, and a collector-region single crystal is produced after which, at a suitable time, donor and acceptor impurities in large quantities are dropped in, and the emitter-region single crystal is pulled up. However, if a base region is to be made by diffusion, the crucible **2** and molten semiconductor **12** cannot be used repeatedly, and, if a pnp-type or npn-type single crystal is to be developed subsequently, the crucible **2** and remaining, molten semiconductor **12** must be changed. Moreover, the aforementioned operations must be repeated anew. For this reason, the time required for the production of a junction crystal is long, and the production of the crystal pulling operation is poor. Especially in the case of germanium or silicon, if the semiconductor material which has once melted is congealed, it will expand during solidification, and the probability of its breaking the quartz crucible **2** is high.

By the process of the present invention, however, if single crystals such as that shown in FIG. 3 are prepared in great numbers, junction crystals as illustrated in FIG. 5 can be produced repeatedly with the molten semiconductor **12** maintained in the molten state by suitably adapting the crystal-pulling device of FIG. 2. By said process moreover, it is possible to produce, in a very short time, the emitter region **14** and base region **13** as indicated in FIG. 5. Accordingly, by providing through a suitable means a large number of single crystal supporting mechanisms **7** and **8** of FIG. 2, by providing a mechanical means capable, by such methods as rotation, of bringing alternately said crystal supporting mechanisms directly over crucible **2**, and by preparing several single crystals **1** and **3** and devising a mechanical means for mounting and dismounting the single crystal, it is possible to produce continuously the junction crystals as illustrated in FIG. 5 at a time rate of one crystal every few minutes to perhaps a certain time somewhat longer. It will be appreciated furthermore, that because it is possible to cut out several hundreds of junction transistor elements from a single piece of single crystal, this process is singularly adaptable and suitable for mass production. It will be appreciated still further that, when a junction type transistor is to be made from the single crystal of FIG. 5, the collector region **14** is cut out of a portion as close to the base domain **13** as possible and used; therefore, the single crystal **3** of FIG. 5 can be used repeatedly

any number of times. From this point also, it may be said that said process is suitable for the mass production of transistors.

Because of the existance of numerous advantages as described above, the process of the present invention has the advantage of being capable of easily mass producing transistors of remarkably improved yield and electrical characteristics and of high cut-off frequency when compared with the conventional, grown diffused process.

In addition to the impurities mentioned in the aforedescribed examples, for germanium, one or more of phosphorus and arsenic which are known as donor impurities and boron, aluminum, and indium which are known as acceptor impurities may be used in suitable combinations. Furthermore, silicon may be used in place of germanium, in which case the particulars relating to the donor and acceptor impurities are the same as those for the case of germanium.

It is possible, of course, to produce not only pnp junctions but also npn junctions.

Furthermore, if the ratio of the diffusion constants of, respectively, the n-type impurity and p-type impurity to be added to the emitter region is relatively close to unity, or if it is necessary to increase further the thickness of base domain created by diffusion, it is possible to grow the crystal of emitter region slowly or, by the heat treatment subsequent to the forming of the single crystal, to increase the thickness of the base domain through the inter-solid diffusion of the impurities from the emitter region towards the collector region, said diffusion being compounded to the aforedescribed diffusion of impurities from the molten semiconductor.

While only two examples of embodiment and mode of operation of the present invention have been described, it should be understood that the process can be performed in many other ways. For example, it is possible, of course, for the process to be performed with several other combinations of other semiconductor materials and substances which are to be mixed therewith to become donor and acceptor impurities. Wherefore, it is to be understood that the details stated herein are not to be construed as limitative of the invention, except insofar as is consistent with scope of the following claim.

We claim:

The method of making npn or pnp junctions, said method comprising:

preparing a melt of a semiconductive material, said melt containing a donor impurity and an acceptor impurity, one of said impurities having a greater diffusion constant than the other of said impurities, said donor impurity and said acceptor impurity being present in said melt in relative proportions such that one of said impurities determines the conductivity of a single crystal produced from the melt;

immersing the lowermost portion of a single crystal of the semiconductive material having an electrical conductivity of the type which corresponds to the conductivity determining type in said melt;

maintaining said melt at a temperature such that thermal equilibrium is established between said melt and said single crystal;

thereafter raising the temperature of said melt by 3 to 10° C. during an interval of not more than 20 seconds during which interval between about 0.2 and 0.5 millimeters of the single crystal is melted;

maintaining said melt and said crystal in thermal equilibrium with one another for about 20 to 30 seconds during which interval said donor impurity and said acceptor impurity diffuse from said melt into the freshly melted portion of said crystal;

and then cooling the furnace containing the melt at a rate of approximately 100° C. per minute, while concurrently resolidifying said freshly melted portion of said melt by pulling the single crystal from said melt so as to form an additional portion below said resolidified portion pulled from said melt on the emerging lower end of said crystal, said additional portion and said resolidified portion having opposite electrical conductivities from one another.

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DAVID L. RECK, *Primary Examiner.*