Dec. 20, 1955 G. K. TEAL 2,727,840

METHODS OF PRODUCING SEMICONDUCTIVE BODIES

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FIG. 1

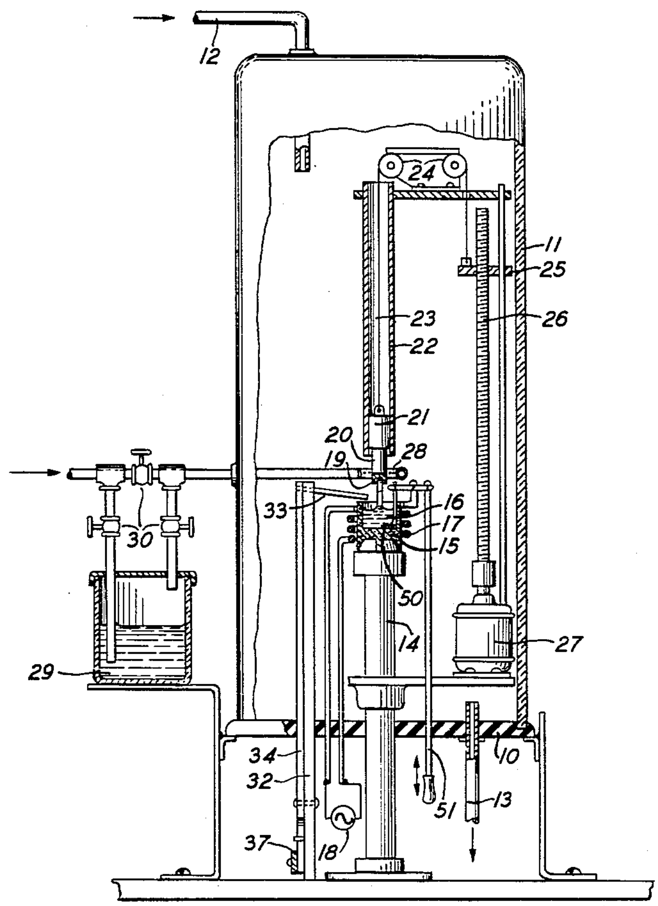
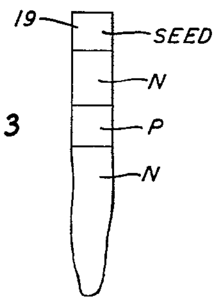


FIG. 3



INVENTOR
G. K. TEAL
BY [signature]
ATTORNEY

METHODS OF PRODUCING SEMICONDUCTIVE BODIES

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FIG. 4

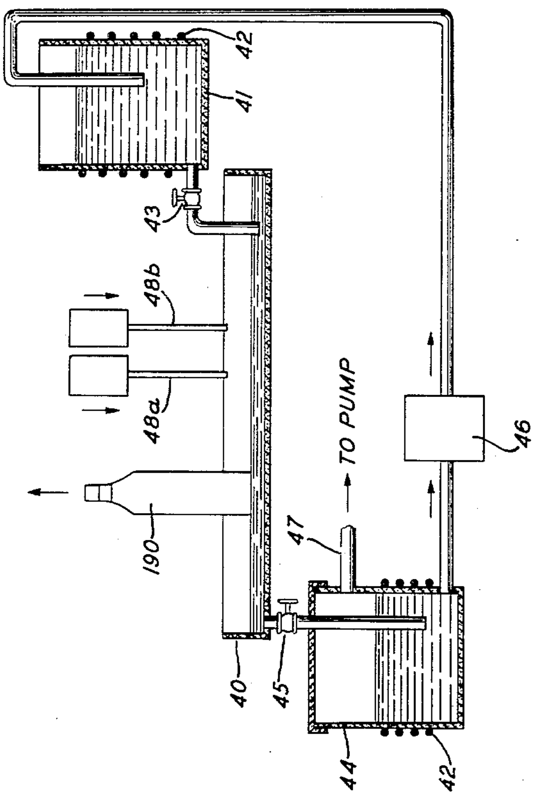
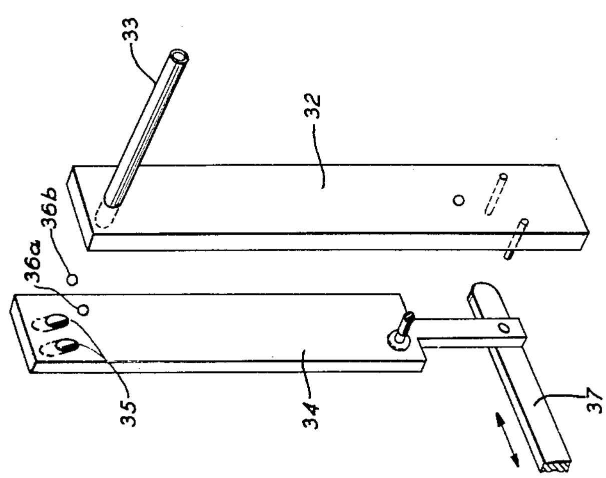


FIG. 2



INVENTOR
G. K. TEAL
BY
ATTORNEY

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METHODS OF PRODUCING SEMICONDUCTIVE BODIES

Gordon K. Teal, Summit, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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8 Claims. (Cl. 148—1.5)

The invention relates to methods of producing semiconductive bodies and more specifically to methods, of the general type disclosed in the application Serial No. 138,354, filed January 13, 1950, now Patent 2,683,676, granted July 13, 1954, of J. B. Little and G. K. Teal, for producing crystals of germanium.

Semiconductive bodies, and particularly those of germanium and silicon, find application in a variety of signal translating devices, such as rectifiers, detectors, modulators and amplifiers. In one type of such devices, of which those disclosed in the application Serial No. 35,423, filed June 26, 1948, now Patent 2,569,347, granted September 25, 1951, of W. Shockley and Patent No. 2,502,479, granted April 4, 1950, to G. L. Pearson and W. Shockley are illustrative, the semiconductive body includes two or more contiguous regions or zones of opposite conductivity types.

The operating characteristics of devices including zones of opposite conductivity types are dependent markedly upon the physical and electrical character of the crystalline material. For example, resistances in such devices are dependent upon the impurity content of the material. Also for example, in semiconductor amplifiers, the efficiency and gain are dependent upon the lifetimes of the charge carriers, viz, electrons in P-conductivity type material and holes in N-conductivity type material. In general, long carrier lifetimes are eminently advantageous.

One general object of this invention is to facilitate and to improve the production of semiconductive bodies and particularly of single crystals of germanium especially suitable for use in signal translating devices.

More specific objects of this invention are to improve the characteristics of such crystals whereby long charge carrier lifetimes are obtained and to enable the production of homogeneous bodies of germanium and silicon, contiguous zones of which have different conductivities or conductivity types, and to enable control or gradation of the conductivity in one or more of such zones or regions in proximity to a P–N junction.

In one illustrative embodiment of this invention, a single crystal of germanium is produced by partially immersing a seed of germanium in a molten mass of germanium material and withdrawing the seed under controlled conditions and at a rate such as to draw some of the mass along with the seed, whereby an elongated crystal or rod of germanium is obtained. The seed and the molten mass may be of the same or opposite conductivity type.

In accordance with one feature of this invention, during the drawing of the elongated crystal or rod, the conductivity or conductivity type of the molten mass is selectively altered in a prescribed manner one or more times, thereby to correspondingly control the characteristics of successive regions or zones of the resulting crystal. For example, in one specific and illustrative case wherein the melt is initially of N-conductivity type germanium material, after a portion of the crystal has been drawn, this portion being of N-conductivity type, an acceptor impurity, such as gallium, is added to the melt in quantities sufficient to change the melt to P type. Hence, the next drawn portion of the crystal is of P type. Later during the drawing of the crystal, a donor impurity, such as antimony or arsenic, is added to the melt to change it to N type whereby the next succeeding portion of the drawn crystal is of this type. Thus, successive contiguous zones or regions of the final crystal are of opposite conductivity types.

Of course, the melt may be initially of P-conductivity type and altered during the growing of the crystal first to N type by addition of a donor impurity and then again to P type by addition of an acceptor impurity. Furthermore, the quantity of the donor or acceptor material added to the melt need not be sufficient to alter the conductivity type of the melt. For example, the quantity may be controlled to alter the conductivity of the resulting crystal as for instance to taper the resistance of either the N or P zone or both on opposite sides of the junction toward or away from this junction.

The invention may be practiced in methods of the general type disclosed in the Little-Teal application identified hereinabove, or in methods such as disclosed in the application Serial No. 138,354, filed January 13, 1950, of M. Sparks wherein a circulated melt is utilized.

The invention and the above-noted and other features thereof will be understood more clearly and fully from the following detailed description with reference to the accompanying drawing in which:

Fig. 1 is an elevational view of apparatus which may be utilized in the practice of the methods of this invention, a portion of the apparatus being broken away and parts being shown in section to illustrate details more clearly;

Fig. 2 is an exploded perspective view of the impurity-introducing mechanism included in the apparatus shown in Fig. 1;

Fig. 3 illustrates a typical crystal of semiconductive material produced in accordance with this invention; and

Fig. 4 is a diagram of another form of apparatus which may be utilized in the practice of this invention.

The invention will be described hereinafter with particular reference to the production of single crystals of germanium by a method involving the use of antimony as a donor impurity and gallium as the acceptor impurity. It is to be understood, however, that the invention may be used also in the production of silicon single crystals and that other donor and acceptor impurities may be utilized. Among the donor impurities which may be used with either silicon or germanium are phosphorus and arsenic as well as intimony and other acceptor impurities which may be utilized are boron, aluminium and indium as well as gallium. The initial material utilized may be silicon or germanium of either conductivity type. Germanium of either conductivity type may be produced in one way as disclosed in the application Serial No. 638,351, filed December 29, 1945, now Patent 2,602,211, granted July 8, 1952, of J. H. Scaff and H. C. Theuerer. Silicon material of either conductivity type may be produced in one way as disclosed in the application Serial No. 793,744, filed December 24, 1947, now Patent 2,567,970, granted September 18, 1951, of J. H. Scaff and H. C. Theuerer.

Referring to the drawing, the apparatus illustrated in Fig. 1 comprises a base **10** having mounted thereon a bell jar **11** provided with inlet and outlet ports **12** and **13** respectively by way of which a suitable gas such as hydrogen or helium may be circulated through the bell jar **11**. Extending inwardly from the base **10** is a standard **14** upon which a crucible **15**, advantageously of carbon for a germanium melt, is mounted. Quartz crucibles may be used for silicon melts. The crucible has therein a charge 16 of semiconductive material, specifically germanium or silicon, of either conductivity type which is liquefied by induction heating through the agency of a coil 17 energized from a high frequency source 18.

Opposite the free surface of the charge or mass 16 is a seed 19 which is carried by a stem 20 extending from a weight 21. The latter is slidable longitudinally in a guide 22 and is suspended by a wire 23 which passes over pulleys 24 and is connected to a platform 25. The platform 25 is mounted threadably upon a drive shaft 26 rotatable by a motor 27. Upon operation of the motor 27 to rotate the shaft 26, the platform 25 is raised or lowered whereby the weight 21 and the seed 19 carried thereby are lowered or raised respectively.

Extending into the bell jar 11 is a pipe having at its inner end a circular portion 28 provided with a multiplicity of apertures through which jets of an appropriate gas may be played upon the material drawn in the manner described hereinafter. The gas may be, for example hydrogen, introduced into the pipe from a source, not shown, and the hydrogen may be caused to contain some water vapor from a reservoir 29 of distilled water coupled to the pipe through a valve system 30.

The apparatus thus far described is generally the same and is operated in the same manner as that disclosed in the application of J. B. Little and G. K. Teal identified hereinabove.

In addition the apparatus shown in Fig. 1 comprises a mechanism shown in greater detail in Fig. 2 for selectively introducing significant impurities into the charge 16 within the crucible 15. This mechanism comprises a first plate 32 having a single aperture therein which is in communication with a spigot 33 extending over the crucible 15. A second plate 34 slidable in face-to-face relation upon the plate 32, is rockable by a lever 37 and has therein a pair of spaced recesses 35 in each of which a pellet 36*a* or 36*b* is positioned. The pellets 36 advantageously are alloys of germanium and a significant impurity, the impurity in one pellet being a donor and that in the other being an acceptor. Either recess 35 may be aligned with the inlet and the spigot 33 by rocking of the plate 34 whereby the pellet contained in that recess passes into the spigot 33 and thence into the charge in the crucible 15.

Disposed in the crucible 15 is a stirrer 50 which may be actuated by manipulation of the rod 51.

In the drawing of the crystal, the charge 16 within the crucible 15 is heated through the coil 17 and maintained in the molten state. The motor 27 is operated to partly immerse the seed 19 into the molten mass and then is operated so that the seed is withdrawn from the mass at a rate to draw some of the molten material along therewith. As set forth in the Little-Teal application above identified, the rate of withdrawal of the seed 19 is made substantially that at which the molten material crystallizes.

The conductivity type of the molten material withdrawn from the crucible will be dependent, of course, upon the donor-acceptor impurity balance in the material. For example, if in the initial charge the donor impurity is in effective excess, the portion of the mass withdrawn will be of N-conductivity type. At a prescribed point in the withdrawing operation, the plate 34 may be manipulated whereby the pellet 36 containing the acceptor impurity is introduced into the melt. The amount of acceptor impurity is made sufficient to change the molten mass to the opposite conductivity type. Thus, as the withdrawal of the seed continues, the next portion of the crystal formed is of P-conductivity type and this portion forms a junction with the first drawn portion. If subsequently the plate 34 is manipulated to introduce into the melt the pellet 36 containing the donor impurity, the mass within the crucible will be changed from P to N conductivity type. The subsequently withdrawn material also will be of N-conductivity type. Thus, by selective introduction of impurities into the melt during the withdrawal of the seed, contiguous zones of opposite conductivity types are produced in the withdrawn material and in the final crystal.

A typical crystal produced in accordance with this invention is illustrated in Fig. 3 and as there shown comprises the seed 19 followed in succession by zones of N-, P- and N conductivity type respectively.

It will be understood, of course, that the charge or mass 16 may be initially P-conductivity type and by introduction of appropriate impurities changed first to N-conductivity type and then again to P-conductivity type. It will be understood further that any desired number of changes in conductivity type of the melt may be effected during the production of a single crystal.

In one specific example illustrative of the invention a germanium body comprising an N–P junction was produced in the following manner: A high purity N type single crystal of germanium was grown in the apparatus illustrated in Fig. 1 in the general manner disclosed in the application of J. B. Little and G. K. Teal identified hereinabove. The initial high purity material was produced by reduction of germanium dioxide in hydrogen in the manner disclosed in the application of J. H. Scaff and H. C. Theuerer also identified hereinabove. During the growth of the N type crystal, the composition of the germanium melt was altered by dropping thereinto a pellet of an alloy of germanium and gallium. The melt was thereby converted from N-conductivity type to P type, whereby the drawn crystal was a rod-shaped germanium single crystal including a transverse P–N junction. The initial germanium material was substantially 50 grams, the P–N junction was located about one-half way down the length of the drawn crystal, and the added alloy was a 20 milligram pellet of 0.2 per cent gallium in germanium.

The total hydrogen flow in the apparatus was approximately 100 cubic feet per hour with about 2 cubic feet per hour from the jets around the growing crystal.

In a typical element including a P–N junction prepared in this manner the resistivity was 6 ohm-centimeters on the N type side of the junction and 0.6 ohm-centimeter on the P type side of the junction. The carrier lifetimes on the two sides of the junction were of the order of 70 to 100 microseconds. These values are substantially equal to those determined for the junction region.

As another example, a germanium element having a P type zone between and contiguous with two N type zones was fabricated in the following manner: First an N section or zone was grown from an N type melt and a pellet of germanium alloy of gallium was dropped into the melt during the growth of the crystal, thereby to produce an N–P junction and a P section or zone in the drawn crystal. Then, specifically a few seconds after introduction of the first pellet, a second pellet of an antimony alloy of germanium was dropped into the melt thereby converting the melt back to N type, whereby an N type section was crystallized. The resultant crystal was a single crystal of germanium comprising a thin P type layer or zone, of the order of 30 mils thick, between two regions or zones of N type germanium.

The environmental conditions during the growth of the P–N–P structure were substantially the same as those set forth hereinabove in the discussion of the exemplary P–N structure. The initial germanium was an ingot of high purity germanium, the first pellet of germanium alloy was essentially the same as that described hereinabove and the second pellet was a 15 milligram pellet of 6.4 per cent antimony in germanium.

The resulting structure was operated as a transistor of the form disclosed in the application of W. Shockley hereinabove identified and exhibited long carrier lifetimes in the transition P type region or zone, exceptionally low noise and high power gains.

The apparatus illustrated in Fig. 4 comprises a trough **40** along which molten semiconductive material, germanium or silicon, is flowed from a reservoir **41** heated as by an induction coil **42**, the reservoir being connected to the trough by way of a valve **43**. The molten material may be discharged to a second reservoir **44** connected to the trough by way of a valve **45**. Circulation may be effected through the agency of a suitable pump **46**. The material in the second reservoir **44** may be purified by passing it through a suitable purification chamber, not shown, connected to the reservoir **44** by ports, one of which is shown at **47**.

A seed **190** is partially immersed in the molten material within the trough **40** and is withdrawn by appropriate mechanism not shown in the same manner as the seed **19** in the embodiment of the invention heretofore described to withdraw some of the molten material therewith. Insertable into the molten material are rods **48a** and **48b** of an alloy of germanium and a significant impurity. For example, the rod **48a** may contain a donor impurity and the rod **48b** an acceptor impurity.

As the seed **190** is withdrawn from the molten material flowing in the trough **40**, the conductivity type of the molten mass may be changed by inserting one or the other of the rods **48** into the mass. Thus, if the mass is initially of N-conductivity type, the acceptor impurity-containing rod is immersed into the mass thereby to change it to P-conductivity type. The P-conductivity type mass may be changed to N-conductivity type by insertion thereinto of the donor impurity-containing rod **48**. Thus, it will be seen that as in the method hereinbefore described with reference to Fig. 1, the conductivity type of successive regions of the material withdrawn from the melt by upward motion of the seed **190** may be altered so that NPN or PNP type single crystals are produced.

Although the invention has been described thus far with particular reference to the alteration of the conductivity type of the molten mass and, hence, of the resulting single crystal, it will be appreciated that by appropriate control of the amount of donor or acceptor impurities introduced into the molten mass, a selective and prescribed change in the conductivity of the material and, hence of successive regions or zones of the final crystal may be realized.

Although the invention has been described with particular reference to introduction of the significant impurity in the solid state, such impurity may be introduced into the melt in other ways, for example in the form of a gas directed against the melt as through a jet, not shown, in proximity to the surface of the melt. Illustrative of the gases which may be employed are boron hydride and antimony hydride.

It will be appreciated also that although specific embodiments of the invention have been shown and described, they are but illustrative and that various modifications may be made therein without departing from the scope and spirit of this invention.

What is claimed is:

1. A method of making a semiconductive element which comprises melting a mass consisting essentially of a predominating conductivity-type determining impurity and semiconductive material selected from the group consisting of germanium and silicon, introducing into a molten mass a seed consisting essentially of the same semiconductive material as in the mass and a conductivity-type determining impurity, withdrawing the seed at a rate to withdraw some of said molten mass along therewith, then without separating the seed and withdrawn material completely from the molten mass, adding a conductivity-type determining impurity to the molten mass to alter the conductivity type of the conductivity-type determining impurity predominating in the molten mass, further withdrawing said seed away from the molten mass at a rate to withdraw an additional portion

of the molten mass, and allowing the withdrawn material to crystallize.

2. The method of making a semiconductive element which comprises melting a mass consisting essentially of a predominating conductivity-type determining impurity and semiconductive material selected from the group consisting of germanium and silicon, introducing into the molten mass a seed consisting essentially of the same semiconductive material as in the mass and a conductivity-type determining impurity, withdrawing the seed at a rate to withdraw some of said mass along therewith, then without removing the seed and withdrawn material completely from the mass adding a conductivity-type determining impurity to the molten mass to control the electrical properties of the material withdrawn, further drawing said seed away from the molten mass at a rate to draw an additional portion of the mass, and allowing the withdrawn material to crystallize.

3. The method of making a semiconductive element which comprises melting a mass consisting essentially of semiconductive material selected from the group consisting of silicon and germanium and a conductivity-type determining impurity such that the material withdrawn from the melt will after solidification be of one conductivity type, introducing into the molten mass a seed consisting essentially of the semiconductive material of the mass and a predominating conductivity-type determining impurity characteristic of the one conductivity type, withdrawing the seed at a rate to draw some of said mass along therewith and to allow the material withdrawn to solidify, then without separating the seed and the withdrawn material completely from the mass adding a conductivity-type determining impurity to the molten mass to alter the conductivity type after solidification of the withdrawn material, and further withdrawing said seed at a rate to draw an additional portion of the mass which is allowed to solidify.

4. The method of making a semiconductive element which comprises melting a mass consisting essentially of semiconductive material selected from the group consisting of silicon and germanium and a conductivity-type determining impurity such that the material withdrawn from the melt will after solidification be of one conductivity type, introducing into the molten mass a seed consisting essentially of the same semiconductive material as in the mass and a predominating conductivity-type determining impurity characteristic of the one conductivity type, withdrawing the seed at a rate to draw some of said mass along therewith and allowing the material withdrawn to solidify, then without separating the seed and the withdrawn material completely from the mass adding a conductivity-type determining impurity to the molten mass to control the electrical properties after solidification of the withdrawn material, and further withdrawing said seed at a rate to draw an additional portion of the mass which is allowed to solidify.

5. The method of making a germanium element which comprises melting a mass consisting essentially of germanium and a predominating conductivity-type determining impurity, introducing into the molten mass a seed consisting essentially of germanium and a conductivity-type determining impurity of the same conductivity type as that in the molten mass, withdrawing said seed away from said mass to uplift material which is allowed to solidify, and then without separating the seed and the uplifted material completely from the mass adding a conductivity-type determining impurity to control the concentration of conductivity-type determining impurities in the mass.

6. The method of making a germanium element which comprises melting a mass consisting essentially of germanium and a predominating conductivity-type determining impurity, introducing into the molten mass a seed consisting essentially of germanium and a conductivity-type determining impurity of the same conductivity type

as that in the molten mass, withdrawing said seed away from said mass to uplift material which is allowed to solidify, and then without separating the seed and the uplifted material completely from the mass adding a conductivity-type determining impurity to the mass of the type opposite to that predominating in the mass to alter the conductivity type after solidification of the material being withdrawn.

7. The method of making a semiconductive crystal having therein contiguous zones of opposite conductivity type which comprises melting a mass of semiconductive material selected from the group consisting of germanium and silicon and a predominant conductivity-type determining impurity, introducing into the molten mass a seed consisting essentially of the same semiconductive material as the mass and a conductivity-type determining impurity of the same conductivity type as that in the mass, withdrawing said seed at a rate to withdraw some of the mass along therewith and to allow the material withdrawn to solidify, and at spaced times in the period of withdrawal adding first to the molten mass a conductivity-type determining impurity of type and quantity so that the conductivity type after solidification of the material being withdrawn is of opposite conductivity type and subsequently a conductivity-type determining impurity of type and quantity so that the conductivity type after solidification of the material being withdrawn is of the original conductivity type.

8. In the production of a monocrystalline element consisting essentially of germanium and a conductivity-type determining impurity, by withdrawing a seed from a molten mass consisting essentially of germanium and a conductivity-type determining impurity at a rate to draw some of the mass along with said seed and to allow the withdrawn material to crystallize, the method which comprises introducing alternately during the period of withdrawal donor and acceptor impurities into the molten mass to alternate the conductivity type after crystallization of successive regions of the withdrawn material.

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