Jan. 10, 1956 W. SHOCKLEY 2,730,470

METHOD OF MAKING SEMI-CONDUCTOR CRYSTALS

Filed June 15, 1950

FIG. 1

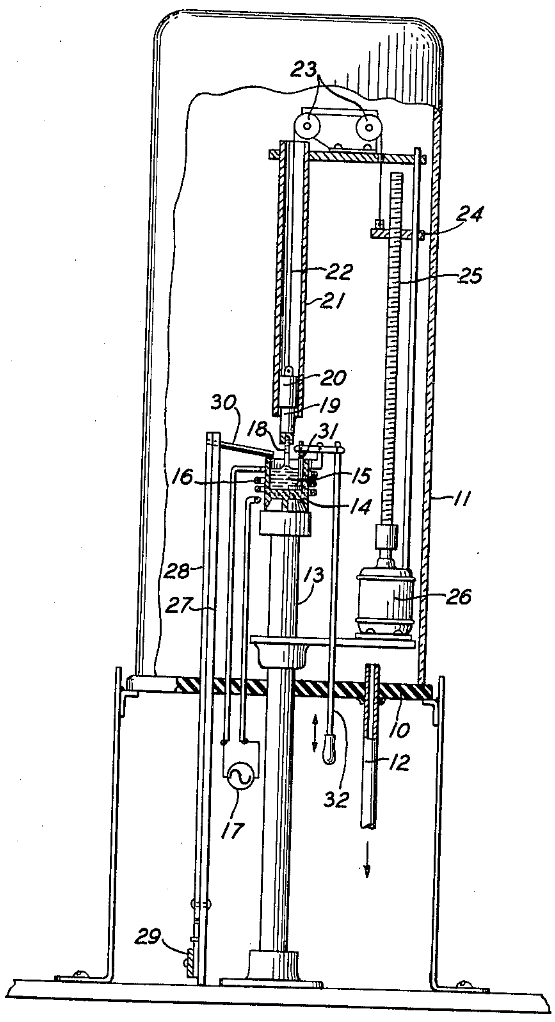
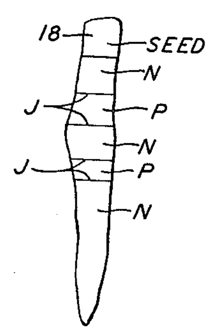


FIG. 2



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2,730,470

Patented Jan. 10, 1956

2,730,470

METHOD OF MAKING SEMI-CONDUCTOR CRYSTALS

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Application June 15, 1950, Serial No. 168,289

2 Claims. (Cl. 148—1.5)

This invention relates to the production of semiconductive bodies or elements and more particularly to methods, of the general type disclosed in the application Serial No. 138,354, filed January 13, 1950, of J. B. Little and G. K. Teal, which issued on July 13, 1954, as United States Patent 2,683,676, for producing single crystals of germanium especially suitable for use in signal translating devices.

The method disclosed in the above-identified application comprises, in general, the insertion of a seed of germanium into a molten mass of germanium material and withdrawing the seed under controlled conditions and at a rate to withdraw some of the molten mass along therewith, thereby to form a homogeneous elongated body or crystal of germanium. As set forth in the application referred to, bodies or crystals produced in accordance with this method have a number of unique characteristics of particular advantage in signal translating devices, such as rectifiers or amplifiers, utilizing such crystals.

In one type of semiconductor signal translating devices, of which those disclosed in the application Serial No. 35,423, filed June 26, 1948, of W. Shockley, now Patent 2,569,347, granted September 25, 1951 are illustrative the semiconductive body comprises two or more contiguous zones or regions of opposite conductivity types. For example, in one particular construction, the semiconductive body comprises an N-conductivity type zone or region between and forming junctions with two zones or regions of P-conductivity type. Further, in a specific type of such device such as disclosed in the application Serial No. 96,059, filed May 28, 1949, of W. Shockley, now United States Patent 2,672,528, granted March 16, 1954, it is advantageous that the conductivity of one or both contiguous zones of opposite conductivity type vary in a prescribed manner from or toward the junction of the zones or regions.

As is now well known, both the conductivity and conductivity type of a semiconductive material are determined by impurities in the material. Donor impurities tend to make the material N-conductivity type whereas acceptor impurities tend to make the material P-conductivity type. These impurities, donor and acceptor, of which examples will be given hereinafter, are designated, and are so referred to hereinafter, as significant or conductivity type determining impurities.

One general object of this invention is to facilitate and to improve the production of germanium crystals having contiguous zones of different conductivity types therein. A more specific object of this invention is to enable the controlled variation of the conductivity or conductivity type, or both, in germanium produced in the general manner above described.

In accordance with one feature of this invention, in the production of a germanium crystal by withdrawing a seed from a molten mass of germanium material, the initial material utilized contains an effective excess of donor or acceptor impurity of a kind which has a boiling point below that of the germanium and which determines the conductivity type of the melt and of the crystal drawn therefrom, and during the withdrawal of the seed the impurity is selectively vaporized whereby the proportion thereof in the molten mass is decreased. Thus, as the crystal is drawn, the conductivity of succeeding portions thereof is altered. The rate of change in conductivity will be dependent of course, upon the rate of evaporation of the impurity. At a desired point in the process, the conductivity type of the molten mass may be made opposite that of the initial mass by introducing thereinto an appropriate impurity whereby following introduction of this impurity the portion of the drawn crystal is of opposite conductivity type to that of the first drawn portion. The added impurity also may be vaporized selectively thereby to produce a prescribed gradation in the conductivity of this portion of opposite conductivity type.

In one specific and illustrative embodiment of this invention, a germanium crystal is drawn from a molten mass having initially a donor impurity, for example antimony therein, and during the drawing of the crystal the antimony is controllably vaporized whereby the conductivity of successive portions of the drawn crystal decreases. Then an acceptor impurity, such for example as gallium, is introduced into the melt in quantities sufficient to convert the melt to P-conductivity type. The temperature of the melt is then altered while drawing of the crystal continues, to vaporize the gallium at a desired rate. Thus, there is produced a single crystal of germanium, successive zones of which are of N- and P-conductivity types, respectively, and wherein the conductivity of each zone is graded with respect to the P-N junction between the two zones.

In another specific and illustrative embodiment of this invention, single crystals of silicon having contiguous P and N zones or regions the resistance of each of which varies in prescribed manner relative to the P-N junction are drawn in like manner as the germanium crystal described above. A suitable donor impurity for use in the case of silicon is phosphorus and suitable acceptor impurities for this case are boron and aluminum.

It will be understood, of course, that the invention may be utilized in the growth of crystals having first a P-section and then an N-section as well as vice versa and that it may be practiced also in the production of single crystals of germanium or silicon having a plurality of P-N junctions therein.

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 practicing this invention, a portion of the apparatus being broken away and parts being shown in section to illustrate details more clearly; and

Fig. 2 illustrates one form of crystal produced in accordance with this invention.

Referring now to the drawing, the apparatus illustrated in Fig. 1 comprises a base **10** mounting a bell jar **11** which may be evacuated to a high degree by way of a port **12** connected to a vacuum pump, not shown. Extending through the base **10** is a pedestal **13** upon which a crucible **14**, advantageously of carbon, is affixed. The crucible contains a charge **15** of semiconductive material, such as germanium or silicon, each of either conductivity type. Suitable germanium material for the charge **15** may be produced for example in the manner 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. Suitable silicon material for the charge **15** 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.

The crucible is encompassed by a coil **16** energized from a high frequency source **17** thereby to melt the charge **15**. Opposite the free surface of the charge **15** is a seed of semiconductive material **18** which is affixed to a stem **19** on a weight **20**. The weight **20** is slidable in a guide **21** and is suspended by a wire **22**. The latter extends over pulleys **23** to a platform **24** mounted threadably upon a rotatable threaded shaft **25** which may be driven in either direction by a motor **26**. As the shaft **25** is rotated, the platform **24** rides therealong to raise or lower the weight **20** and the seed **18**.

Also extending from the base **10** are a pair of plates **27** and **28**, the plate **28** being over the plate **27**, in face-to-face relation therewith, by operation of a lever **29**. The plate **27** has therein a single aperture from which a spout **30** extends over the crucible **14**. The plate **28** has therein two or more recesses arranged to be aligned individually with the aperture in the plate **27** by movement of the plate **28**. These recesses contain pellets of an alloy of semiconductive material and a donor or acceptor impurity. Details of the plates **27** and **28** and the manipulation thereof are set forth more clearly in the application Serial No. 168,184, filed June 15, 1950, of G. K. Teal.

Extending into the crucible **14** is an agitator element **31** manipulable from the exterior of the bell jar by a rod **32**.

The operation of the apparatus is generally similar to that disclosed in the application of J. B. Little and G. K. Teal hereinabove identified. In brief, the semiconductive seed **18** is partly immersed in the molten charge **15** and then is withdrawn from the charge or mass **15**, as a result of operation of the motor **26**, at a rate to withdraw some of the molten mass along with the seed and such that the withdrawal rate is substantially the same as the crystallization rate of the semiconductive material being withdrawn.

As has been indicated hereinabove, the charge or molten mass **15** may be of either conductivity type. For example, it may be of germanium (with a boiling point of approximately 2700° C.) containing antimony (with a boiling point of approximately 1380° C.) whereby it is of N conductivity type. In accordance with a feature of this invention, concomitantly with the withdrawal of the seed, the molten mass is heated to a temperature such that selective vaporization of the antimony from the mass obtains. Thus, successive regions of the mass withdrawn along with the seed contain less and less of the significant impurity, namely antimony in the specific case under discussion, whereby a tapering of the resistivity of the withdrawn mass and hence of the formed crystal is realized. The extent of the taper or variation in resistivity will be dependent, of course, upon the rate of vaporization of the impurity. The rate of vaporization of antimony will be dependent upon the temperature. Some vaporization of antimony obtains at the temperature requisite to maintain the mass molten and the rate of vaporization of this impurity increases as the temperature is increased.

At a desired time in the withdrawing step, the conductivity type of the molten mass may be changed by dropping thereinto a pellet of germanium alloy containing an impurity of the opposite type. Thus, for example, the plate **28** may be manipulated to introduce into the N conductivity type mass or charge **15** a pellet of alloy of germanium and gallium. Gallium is an acceptor impurity (with a boiling point of approximately 1600° C.) and upon melting of the pellet in the mass will convert the N-type mass to P type. Hence, as the withdrawal of the seed continues, the withdrawn material is of P conductivity type and there is thus produced in the resulting crystal a P–N junction. The charge containing the gallium may be heated through the agency of the source **17** to an appropriate temperature to vaporize gallium from the melt whereby throughout the P-type portion of the withdrawn material a taper in resistivity is effected.

The conductivity type of the charge or mass subsequently may be changed again by introducing into the mass a donor impurity. For example, this may be effected by introducing into the mass a pellet of an alloy of germanium and antimony. The antimony then may be vaporized to control the resistivity of the N-type material withdrawn following the P-type zone or region in the crystal. Hence, it will be appreciated that a single crystal of germanium having a P-type zone between and contiguous with two N-type zones may be produced.

Conversely, the charge **15** may be initially of P conductivity type and during drawing of the crystal changed first to N conductivity type and then again to P conductivity type by introduction of appropriate donor and acceptor impurities, respectively, thereinto, whereby a crystal having an N-type zone between and contiguous with two P-type zones is produced.

Although in the specific example above described antimony and gallium were set forth as the donor and acceptor impurities, respectively, it will be appreciated that other donor impurities such as phosphorus and arsenic having boiling points of 280° C. and 615° C., respectively and other acceptor impurities such as boron, aluminum, and indium having boiling points of 2500° C., 1800° C. and 1450° C., respectively may be utilized also. Although germanium has been set forth in this case as the semiconductive material, silicon with a boiling point of 2600° C. may be used with any one of or combinations of the donor and acceptor impurities above mentioned.

It will be appreciated also that the conductivity type of the molten mass may be changed a multiplicity of times during the drawing of the crystal to produce in the final crystal a series of P-N junctions.

A typical crystal produced in accordance with the method of this invention is illustrated in Fig. 2 and comprises the seed **18** followed by N and P zones as indicated, adjacent zones forming P-N junctions J.

Although specific embodiments of this invention have been described, it will be understood that 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. The method of making a semiconductive crystal which comprises melting a mass of semiconductive material selected from the group consisting of germanium and silicon and containing a conductivity type determining impurity having a boiling point below that of said material, inserting a seed of said material into said mass, withdrawing said seed at a rate to withdraw some of said mass along therewith, concomitantly with the withdrawal of said seed increasing the temperature of the remaining mass thereby to increase the rate of vaporization of said impurity therefrom and reduce the concentration of said impurity in the remaining mass, continuing withdrawal of said seed at said rate following said increasing of the temperature, and cooling the withdrawn material to solidification.

2. The method of making an elongated crystal of germanium having a resistivity which varies progressively along the length of the crystal, said method comprising melting a mass of N conductivity type germanium containing antimony, inserting a seed of germanium into said mass, withdrawing said seed at a rate to withdraw some of said mass along therewith, during withdrawal of said seed increasing the temperature of the remaining mass thereby to accelerate the rate of vaporization of antimony therefrom, continuing withdrawal of said seed at said rate following said increasing of the temperature, and cooling the withdrawn material to solidification.

References Cited in the file of this patent

UNITED STATES PATENTS

2,402,582 Scaff ---------------- June 25, 1946

(Other references on following page)

UNITED STATES PATENTS

2,447,829	Whaley	Aug. 24, 1948
2,449,484	Jaffe	Sept. 14, 1948
2,504,628	Benzer	Apr. 18, 1950
2,505,633	Whaley	Apr. 25, 1950
2,514,879	Lark-Horovitz et al.	June 11, 1950
2,631,356	Sparks et al.	Mar. 17, 1953

FOREIGN PATENTS

625,102	Great Britain	June 22, 1949

OTHER REFERENCES

Holden: "Preparation of Metal Single Crystals," Preprint No. 35 for American Society for Metals (1949), 28 pp.