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METHOD OF PRODUCING SEMICONDUCTIVE BODIES

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This invention relates to the production of semiconductor elements or bodies 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, now Patent 2,683,676, granted July 13, 1954, for producing single crystals of germanium and silicon.

In methods of the general type disclosed in the above-identified application, a seed of semiconductor material is partially immersed in a molten mass of semiconductor material and is then withdrawn therefrom under controlled conditions, at a rate to draw some of the mass along therewith whereby an elongated body or rod of the material is produced. In some cases, for example, as disclosed in the application Serial No. 168,184, filed June 15, 1950, of G. K. Teal, during withdrawal of the seed the conductivity or conductivity type of the molten mass is altered selectively by introducing into the mass a significant impurity, i. e., a donor or acceptor thereby to controllably and selectively alter the electrical characteristics of the portion of the mass withdrawn with the seed at any particular time.

The operating characteristics of semiconductor signal translating devices are dependent markedly upon the quantity and distribution of the significant impurities in the semiconductor material. For example, the resistivity of the body of such material and the characteristics of a junction between the body and a metallic contact there-to vary significantly with the content and concentration of such impurities both in the body and the region at and in the vicinity of the contact. Thus, in the fabrication of semiconductor elements for use in such devices and in the preparation of ingots or large bodies or crystals from which such elements are subsequently cut, it is desirable that the content of impurities be uniform throughout the element or ingot or that the distribution of the impurities vary in a prescribed manner.

One general object of this invention is to improve the quality and uniformity of the product of semiconductor bodies particularly suitable for use in signal translating devices. More specifically, objects of this invention are to facilitate the realization of homogeneous impurity content throughout such bodies or prescribed zones or regions thereof and to expedite the attainment of a pre-assigned distribution of the impurities throughout the bodies or such zones or regions.

In accordance with one feature of this invention, in a method of the general type disclosed hereinabove for the production of semiconductor bodies, the molten semiconductor material is caused to flow through a trough or container past the seed and the impurity content in the flowing material is controlled to obtain either a homogeneous or preassigned varying impurity content and distribution in the material flowing past the seed being withdrawn. The type of either the impurity in the molten mass or of the impurity which is in effective excess in the mass may be controlled or altered by inserting into the flowing material upstream from the seed an alloy of the semiconductor material and a significant impurity. For example, the conductivity or conductivity type of a mass initially of N-conductivity type may be altered by introducing therein an alloy of the semi-

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conductive material and an acceptor impurity, thereby to convert the mass and the material being withdrawn with the seed to P-conductivity type. Conversely, if the flowing mass is of P-conductivity type it may be converted to N-conductivity type by introducing therein an alloy of the semiconductor material and a donor impurity such as antimony.

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 the single figure is an elevational view, partly diagrammatic, of apparatus illustrative of that which may be utilized in practicing this invention.

Referring now to the drawing, the apparatus therein illustrated comprises a body 10, for example of an insulating material such as a ceramic and a bell jar 11 seated upon and sealed to the base 10 and defining therewith a chamber through which a suitable gas, such as hydrogen or helium, may be passed by way of ports 12. Mounted upon the base 10 by supports 13 is an elongated dish or trough 14 connected at opposite ends to a reservoir 15 and a tank 16 by way of valves 17 and 18, respectively. The reservoir and tank 15 and 16 are encompassed by heating coils 19 and 20, respectively coupled to high frequency power sources 21 and 22, respectively, whereby the material in the reservoir and tank may be heated as will be described hereinafter.

The tank 16 and reservoir 15 may be connected by piping 23 and 24 and a suitable circulating device 25 to provide a closed circulating system.

Particularly advantageously the trough 14, reservoir 15, tank 16 and the piping and valving associated therewith are of a material such as carbon which will not introduce contaminants or impurities into the material utilized.

The tank 16 is sealed against the atmosphere and may be provided with an outlet port 26 leading to a pump, not shown, for purposes which will appear presently.

Mounted adjacent the tank or trough 14 is a removable support 27 having affixed thereto a plurality of semiconductor seeds 28. The support 27 may be raised or lowered relative to the tank or trough 14 by a suitable mechanism not shown. Also mounted in juxtaposition to the trough 14 are a pair of rods 29A and 29B of an alloy of the material being operated upon and a significant impurity, i. e., a donor impurity such as phosphorus, arsenic or antimony or an acceptor impurity such as boron, aluminum, gallium or indium. The significant impurity in the two rods 29A and 29B may be different, that in one rod being a donor and that in the other an acceptor. The two rods are supported by holders 30 which may be raised or lowered individually with respect to the trough 14 by a suitable mechanism not shown.

In the operation of the apparatus, a charge of semiconductor material, specifically germanium or silicon of which the elements or crystals are to be drawn is produced in the reservoir 15. Suitable germanium material may be prepared in the manner disclosed in the application Serial No. 638,351, filed December 29, 1945, of I. Scaff and H. C. Theuerer, now Patent 2,602,211, granted July 8, 1952 and suitable silicon material for the same may be produced in the manner disclosed in the application Serial No. 793,744, filed December 24, 1947, of I. Scaff and H. C. Theuerer, now Patent 2,560, granted September 18, 1951. The operating chambers are flushed with an inert gas such as nitrogen and, if desired, a suitable gas such as hydrogen or helium is circulated through the chamber through the ports 12. The chamber of the reservoir 15 then is heated through agency of the coils 19 to liquefy it, and the molten mass is flowed through the trough or dish 14.

The holder 27 is lowered to partially immerse the seeds 28, which advantageously are of the same material as the molten mass, into the latter, and then to withdraw the seeds therefrom at a rate to draw some of the mass along therewith, the rate of withdrawal being substantially equal to the rate of crystallization of the molten mass. Thus, an elongated rod or crystal of semiconductive material is produced adherent to each of the seeds 28.

The conductivity or conductivity type of the molten material will be dependent, of course, upon the significant impurities therein. This may be selectively altered in a controlled manner by introducing either or both of the rods 29A and 29B into the mass. For example, if the mass is initially of N-conductivity type, it may be converted to P-conductivity type by inserting thereinto the rod, say 29B, containing acceptor impurities. Conversely, the mass if of P-conductivity type may be converted to N-conductivity type by inserting thereinto the rod, say 29A, containing the donor impurity. The material withdrawn along with the seeds 28 will, of course, be of the conductivity type of the mass. The conductivity type may be altered one or more times during withdrawal of the seeds whereby successive contiguous zones of the drawn crystal are of opposite conductivity types and one or more P-N junctions are produced in the resulting crystals. Rod 29A could, for example, be of an alloy of 98 per cent germanium and 2 per cent antimony; rod 29B could be 98 per cent germanium and 2 per cent gallium.

After passing through the dish or trough 14, the molten material flows into the tank 16 and there may be heated through the agency of the coil 20 to vaporize the impurities therefrom, the impurities being removed from the tank by the operation of the pump connected to the outlet 26.

The molten material may be circulated continuously through the system. Alternatively, the flow of material from the dish or trough 14 may be stopped at any time by closing the valve 18, whereby the conductivity and conductivity type of the material withdrawn along with the seeds will be that of the molten mass in the trough 14 at that time.

As an example the rate of flow in the trough might be 0.004 cubic centimeter per second for a crystal 1.0 centimeter diameter growing at the rate of 0.002 centimeter per second.

It is to be noted that flow of the material in the trough or dish 14 effects a mixing thereof so that homogeneity of composition of the material withdrawn with the seeds results. Thus, uniformity of significant characteristics of the crystals produced is realized. Further, the volume of molten semiconductive material in the trough or dish 14 may be relatively small whereby its conductivity or conductivity type may be altered readily, slowly or abruptly. Slow changes in the significant impurity content will produce corresponding gradations in the conductivity of the crystal drawn. Sharp changes in this content are reflected promptly in the material being withdrawn so that sharp P-N junctions are produced. Similarly, by abrupt alteration in the impurity in effective excess, thin zones or regions of either conductivity type may be produced in the drawn crystals, such zones or regions abutting a zone of the opposite conductivity type or being between contiguous with two zones of the opposite conductivity type. For example, a thin P zone may be produced between two N zones. Moreover, the volume of semiconductor material in the reservoir 15 may be large enough to produce a large number of crystals, or crystals of large, or both, may be produced with dispatch.

Although a specific embodiment of this invention has been shown and described, it will be understood that it is illustrative, and that various modifications may be made without departing from the scope and spirit of this invention.

What is claimed is:

1. The method of producing a semiconductive body containing a P-N junction therein which comprises introducing a seed into a molten mass of semiconductive material of one conductivity type and selected from the group consisting of silicon and germanium, said seed being of like material to that of said molten mass, causing the mass to flow laterally past said seed and in contact therewith, withdrawing said seed from said mass at a rate substantially equal to the rate of crystallization of the withdrawn material, and, during the withdrawing step, introducing into the molten mass, upstream from said seed an impurity capable of altering the conductivity type of said mass.

2. The method of producing a semiconductive body containing a PN junction therein, which comprises providing a molten mass consisting essentially of material selected from the group consisting of germanium and silicon and a conductivity type determining impurity, introducing a seed essentially of said material into said mass, causing said mass to flow laterally past said seed, withdrawing said seed from said mass to draw some of said mass along therewith at a rate substantially equal to the crystallization rate of the withdrawn material, introducing into said mass upstream from said seed a conductivity type determining impurity of the type opposite to that in the mass, and continuing the withdrawing step to form a zone in the withdrawn material of conductivity type opposite to that first produced.

3. The method of producing a semiconductive body having a zone of one conductivity type intermediate between zones of opposite conductivity type which comprises providing a molten mass of material selected from the group consisting of germanium and silicon and a first conductivity type determining impurity, introducing a seed of said material into said mass, causing said mass to flow laterally past said seed, withdrawing said seed from said mass to draw some of the mass along therewith at a rate substantially equal to the crystallization rate of the withdrawn material, continuously introducing into said mass upstream from said seed a second conductivity type determining impurity of type opposite to that originally in the mass for changing the conductivity type of the withdrawn material being crystallized, continuing the withdrawing step to form a zone in the withdrawn material of desired thickness, and substituting for the addition of the second impurity an impurity of type similar to the first impurity while continuing the withdrawing step to form crystalline material of conductivity type similar to that of the crystalline material first produced.

4. The method of producing a semiconductive body containing a series of PN junctions, formed by introducing into a molten mass consisting essentially of a conductivity type determining impurity and a material selected from the group consisting of germanium and silicon a seed of like material, causing the mass to flow laterally past said seed and in contact therewith, alternately introducing into said mass upstream from said seed impurities of different conductivity types, and withdrawing said seed from said mass at a rate substantially equal to the rate of crystallization of the withdrawn material, whereby the conductivity type of the material crystallized changes alternately.

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