May 21, 1957 R. EMEIS 2,793,103

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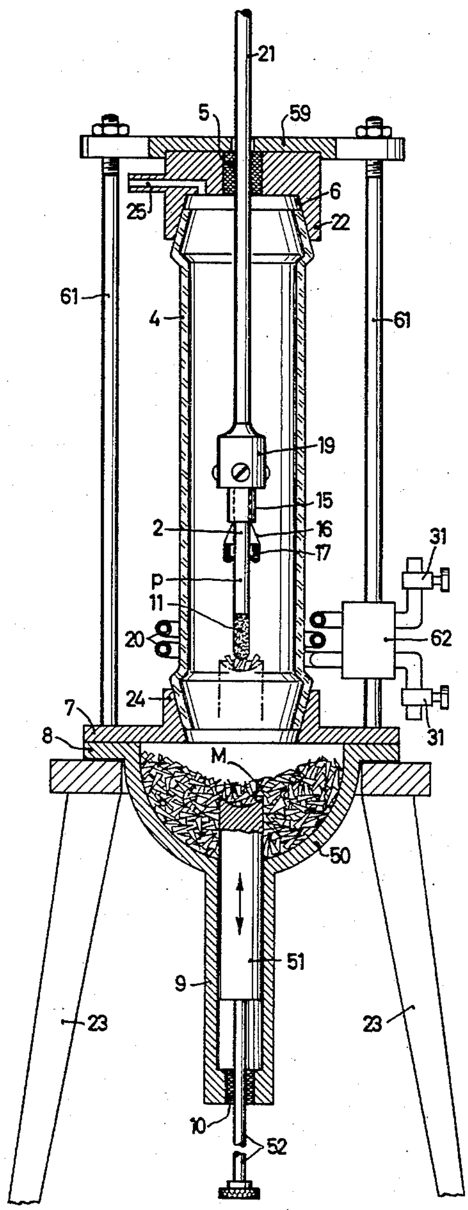
Filed Feb. 18, 1955



United States Patent Office

2,793,103

Patented May 21, 1957

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METHOD FOR PRODUCING ROD-SHAPED BODIES OF CRYSTALLINE MATERIAL

Reimer Emeis, Pretzfeld, Germany, assignor to Siemens-Schuckertwerke Aktiengesellschaft, Berlin-Siemensstadt, Germany, a German corporation

Application February 18, 1955, Serial No. 489,155

16 Claims. (Cl. 23—301)

My invention relates to the production of crystalline materials of high purity or the conversion of such materials into monocrystals, and in a more particular aspect to the processing of electrically semiconducting elements such as germanium and silicon, or of semiconducting compounds of elements from the third and fifth group of the periodic system such as InAs and InSb, and semiconducting compounds of elements from the second and sixth periodic group such as ZnS and HgTe.

Various methods are known for producing rod-shaped bodies from such semiconducting substances. The method of "pulling" a crystal from a melt by placing a crystal seed or germ into contact with the melt and then withdrawing the crystal germ in accordance with the rate of crystal growth, requires an unfavorably large quantity of material being kept molten in a crucible. According to the so-called "zone melting method," a powdered mass of the substance is placed in an elongated crucible (boat) and a longitudinally limited zone of the mass is liquefied and gradually advanced from one end to the other of the crucible so that the entire mass is progressively melted and solidifies into a crystalline or mono-crystalline body. The process also has a purifying effect for the reason that impurities segregate out of the resolidifying material and accumulate in the progressing melted zone so that they become concentrated in the last-solidifying end portion which can be severed off the body. This method, however, leaves much to be desired. The crucible, in certain cases, is not sufficiently heat resistant at the high processing temperatures required, for example, for the melting of silicon. The processed material, after solidification may strongly adhere to the crucible; and, in both methods described, there is also the danger of undesirable impurities newly entering into the material from the walls of the crucible.

According to another known process, rod-shaped bodies of pressed and sintered semiconductor particles, with or without a suitable binder, are held at each end in a vertical position and then heat-treated from one end to the other by progressive zone melting. No crucible is required, but the necessity of first producing the sintered rods involves considerable additional work.

It is an object of my invention to avoid the above-described disadvantages of the known methods by eliminating both the use of a crucible and the necessity of first pressing and sintering a rod-shaped body of the powdered material to be processed.

To this end, and in accordance with a feature of my invention, the process is started with a short piece or stub of crystalline material to act as a crystal germ. This member is vertically supported from above so that its lower end is free. The lower end is locally heated to molten temperature, preferably electrically by radiation or electrical induction. Then the melted end is continually supplied with more of the material in more or less fine-granular form. At least some of the granular material adheres to the liquid material and is melted into the molten end of the stub member. As more and

more of the supplied material is taken up, the stub member progressively lengthens into the shape of a rod. Simultaneously the member or rod and the heating locality are axially displaced relative to each other to always keep the lower end molten and to allow the adjacent upper newly-added zone of material to solidify. In this way a continuously lengthening rod of pure semiconductor material is produced at the lower end of the germinative member. The downwardly hanging position of the rod thus formed is especially advantageous because the drop-shaped zone of molten material at the lower end will adhere more securely, in larger quantity and more uniform shape than a molten dome-shaped zone on top of a rod held upright from below.

The foregoing and other objects, advantages and features of the invention will be apparent from the following description taken in conjunction with the accompanying drawing showing a vertical view, partly in cross section, of a processing apparatus according to the invention.

The illustrated apparatus can be used not only with powder material but also with granular material of any desired grain within a wide range of sizes. A short crystalline stub 2 of the same material is enclosed within a quartz cylinder 4 and is suspended in a vertical position from its upper end by means of a holder 19 fixed to the lower end of a vertical shaft 21. The shaft 21 extends through a vacuum-seal bushing 5 fixed in the center of a socket 22. The upper end of the quartz cylinder 4 is sealed against a beveled circular recess 6 in socket 22. The shaft 21 is independently rotatable and vertically movable in socket 22. The socket 22 is provided with a nipple 25 having a channel communicating with the inside of the quartz cylinder 4 to permit evacuating the cylinder or filling it with a suitable protective gas.

A supporting socket 24 engages the lower end of the quartz cylinder 4 and has an integral annular flange portion 7 against the underside of which is secured the corresponding flange 8 of a funnel-shaped storage container 50. The container has a downwardly extending cylindrical neck 9 fitted with a perpendicularly movable piston 51. A shaft 52, fixed to the lower end of the piston 51, is provided for reciprocating the piston. A sealing bushing 10 is fitted within the neck portion 9 to seal the apparatus at the point where the shaft 52 enters. The vacuum-sealing sockets 22 and 24 are pressed together by means of a plurality of bolts 61 extending between the flange portion 7 and a top plate 59 seated upon the socket 22. The entire apparatus rests upon a circular pedestal 23.

A heating coil 20 surrounding the quartz cylinder at its lower end is provided as a heat source. The coil 20 preferably is of copper tubing to be traversed by cooling water. The ends of coil 20 are connected with respective terminals by means of which the output circuit of a supply of a high-frequency current of several thousand kilocycles (not illustrated) can be connected. The heating coil 20 is preferably fixed with respect to the rest of the apparatus by means of an insulating clamping plate 62 secured to one of the bolts 61.

For starting a melting process, the short starting stub 2 must be preheated. To this end, a ring of tungsten, molybdenum or similar high-melting metal encircles the vicinity of the lower end of the germinative stub 2. The ring 17 is supported by thin wires 16 of heat resistant material. The upper ends of the wires 16 are clamped together with the upper end of the stub 2 in a small quartz tube 15 securely fastened in the holder 19. Obviously, this clamping of wires permits adjustment.

When beginning a crystal-forming process, the holder 19 together with the crystal germ or stub 2 is first lowered by means of shaft 21 so that the lower end of the stub

2 as well as the preheating ring 17 are within the field of the heating coil 20. Upon energizing the heating coil 20 with high frequency current, the preheating ring 17 will become red hot. This raises the temperature locally at the end of the germ stub 2. As a result, the electric conductance of the stub end increases so that induced currents sufficient to bring the stub end to molten temperature will be produced by coil 20. The molten end of the germ stub, for instance when processing silicon, which characteristically has a high surface tension, will assume an axial length of between 5 to 10 millimeters.

The material M in the storage container 50 can be used in the form of the needle-shaped granules resulting from conventional chemical purifying processes. This obviates the otherwise required pulverizing operations.

The contacting of the molten lower end of the germinative stub 2 with the crystalline particles M in container 50 is accomplished by moving the piston 51 from its lowermost position to the position shown in dot-and-dash lines. Some of the particles are then caught in the concave portion at the upper end of piston 51 and are lifted into contact with the melt. A few of the particles then adhere to, and are melted into the drop of liquid material so that the end 11 of stub 2 increases its axial length. Thereupon, the rod 21 is slightly raised so that the molten end portion 11 always remains at the locality of the induction field. The process is continued in this fashion until the desired length of crystalline rod P is produced. The process was found to progress at a growth rate in the order of about 0.5 to 5 millimeters per minute.

Instead of using the moving piston 51 for transporting the semiconductor particles to the molten end 11 of the crystal rod being formed, the holder 19 may be made displaceable to permit rapidly lowering the crystal body into the material M and returning it to the position where the molten end is properly positioned within coil 20 for heating.

The invention is generally applicable to the processing of crystalline substances, including those of the electrically semiconducting type. Aside from elementary semiconductors such as Ge and Si, the invention is well suited for the processing of semiconductor compounds such as AlN, AlP, AlAs, AlSb, GaN, GaP, GaAs, GaSb, InP, InAs, InSb, BP, HgSe, ZnS, CdTe, HgTe.

Crystalline or monocrystalline bodies of semiconductor substance made by the method and apparatus herein described can readily be cut into suitable sizes for the manufacture of electrical devices such as detectors, rectifiers, transistors, varistors, photocells and the like.

It will be obvious to those skilled in the art, upon study of this disclosure, that my invention permits of various modifications other than those specifically illustrated and described without departing from its spirit and scope as defined by the annexed claims.

I claim:

1. The method of producing a rod-shaped member of crystalline material, which comprises suspending a stub of said material in a vertical position and with a lower free end, heating, at a fixed zone, the lower free end of said stub to form a molten drop of said material thereon, repeatedly contacting the molten drop on the lower end of said stub with solid phase granules of said material so that they adhere to the stub, a plurality of said granules being successively melted on said lower end to increase the length of the body, and changing the position of said stub with respect to said heating zone axially so as to heat the lower end of said increased length and allow the previously melted material to solidify.

2. The method defined in claim 1 in which the material is silicon.

3. The method defined in claim 1 in which the material is germanium.

4. The method defined in claim 1 in which the material is taken from the group consisting of the elements germanium and silicon and of semiconducting compounds of elements taken from both the third and fifth group of the periodic system and from both the second and sixth group of the periodic system.

5. The process defined in claim 1 in which the granular solid phase particles are raised into contact with the molten drop on the lower free end of the stub.

6. The method of producing a rod-shaped member of crystalline material, which comprises suspending a stub of said material in a vertical position and with a lower free end, heating, at a fixed zone, the lower free end of said stub to form a molten drop of said material thereon, repeatedly contacting the molten drop on the lower end of said stub with solid phase granules of said material so that they adhere to the stub, a plurality of said granules being successively melted on said lower end to increase the length of the body, and changing the position of said stub with respect to said heating zone axially so as to heat the lower end of said increased length and allow the previously melted material to solidify, the possibility of entry of undesired impurities into the body being minimized by employing only radiative and inductive heating in the process, the molten part of the body being isolated from contact with all foreign bodies including the surfaces of the radiative and inductive heating elements.

7. The method of producing a rod-shaped member of crystalline material which comprises holding a germinative stub member of said material vertically from above, locally heating the lower free end to form a molten lower end, repeatedly dipping said molten end of the stub member into a supply of solid particles of the material, the solid particles adhering to and being suspended from the molten end of the stub, and progressively raising the stub to increase the distance between the upper end of said stub and the heating locality.

8. The method of producing a rod-shaped semiconductor body of crystalline material, which comprises the steps of holding a stub of said material from its upper end in an erect position, heating the lower end of said stub in a heating zone to form a molten lower end, and intermittently adding to said molten lower end a supply of said material in comminuted form and melting said supply on said lower end in said heating zone to progressively increase the length of the body, and axially displacing the stub with respect to the said heating zone to allow the previously melted material to solidify and to maintain the lower molten end in the heating zone, said steps being carried out in a neutral atmosphere.

9. The method of producing a rod-shaped body of crystalline material, which comprises suspending a stub of said material from above in a vertical position, heating only the lower end of said stub in a heating zone to form a molten lower end, and contacting the molten lower end with granular solid phase particles of said material by lifting the material to the molten lower end, the said solid particles adhering to and being suspended from the lower molten end, and melting said particles on said end in said heating zone to increase the length of the body, and raising the stub to maintain the lower end in said heating zone.

10. The method of producing a rod-shaped member of semiconductor crystalline material in which the possibility of entry of undesired impurities into said material is minimized, which comprises holding a germinative stub member vertically from above, locally heating by heat radiation and electro-induction in a heating zone the lower free end to form a molten lower end, at intervals causing the contact of the molten free end of said stub member with a supply of solid phase particles of the material which adhere to and are suspended from the molten end, melting the adhering particles in said heating zone, and progressively increasing the distance between the upper end of said stub and the said heating zone to allow the previously melted material to solidify.

11. The method of producing a rod-shaped semiconductor body of crystalline material, which comprises the

steps of holding a stub of said material from its upper end in an erect position, heating the lower end of said stub in a heating zone to form a molten lower end, and intermittently adding to said molten lower end a supply of said material in comminuted form, in solid phase, and melting said supply on said lower end in said heating zone, to progressively increase the length of the body, and axially displacing the stub with respect to the said heating zone to allow the previously melted material to solidify and to maintain the lower molten end in said heating zone, said steps being carried out in a neutral atmosphere, the material being taken from the group consisting of the elements germanium and silicon and of semiconducting compounds of elements taken from both the third and fifth group of the periodic system and from both the second and sixth group of the periodic system.

12. The method of producing a rod-shaped semiconductor body of crystalline material, which comprises suspending a stub of said material from above in a vertical position, heating only the lower end of said stub in a heating zone to form a molten lower end, and contacting the molten lower end with granular solid phase particles of said material, the said solid particles adhering to and being suspended from the lower molten end, and melting said particles on said end in said heating zone to increase the length of the body, and axially displacing the stub with respect to the said heating zone to allow the previously melted material to solidify and to maintain the lower molten end in the said heating zone, the possibility of entry of undesired impurities into the body being minimized by employing only radiative and inductive heating in the process, the molten part of the body being isolated from contact with all foreign bodies including the surfaces of the radiative and inductive heating elements.

13. The process defined in claim 12 in which the material is silicon.

14. The process defined in claim 12 in which the material is germanium.

15. The process defined in claim 12, the material being taken from the group consisting of the elements germanium and silicon and of semiconducting compounds of elements taken from both the third and fifth group of the periodic system and from both the second and sixth group of the periodic system.

16. The process defined in claim 12 in which the granular solid phase particles are raised into contact with the said molten lower end of the stub and the material being taken from the group consisting of the elements germanium and silicon and of semiconducting compounds of elements taken from both the third and fifth group of the periodic system and from both the second and sixth group of the periodic system.

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