Sept. 19, 1967 M. HEIM 3,342,161

APPARATUS FOR PYROLYTIC PRODUCTION OF SEMICONDUCTOR MATERIAL

Original Filed Nov. 27, 1961 2 Sheets-Sheet 1

Fig.1

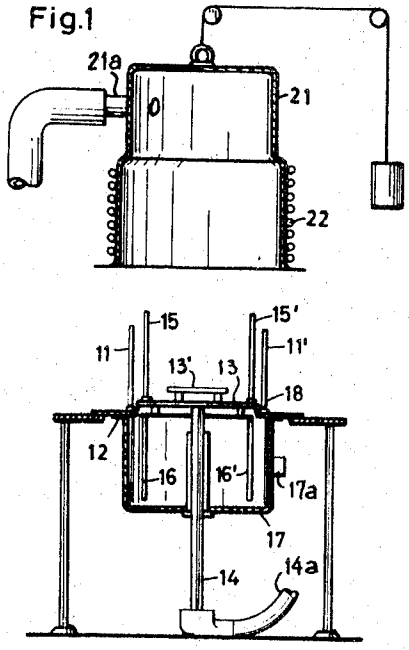


Fig.2

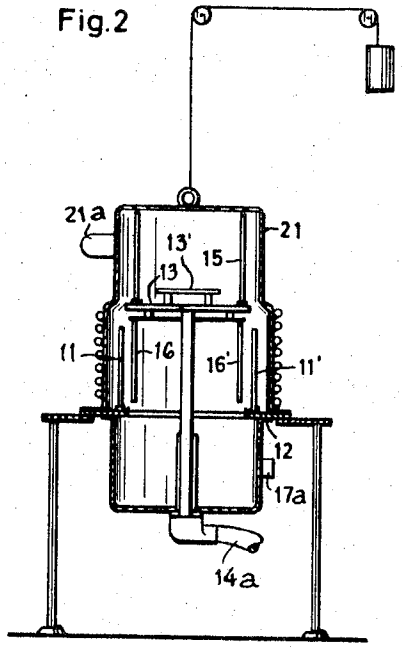


Fig.3

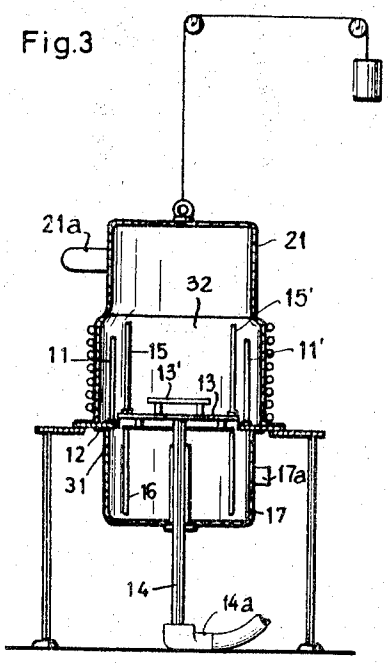
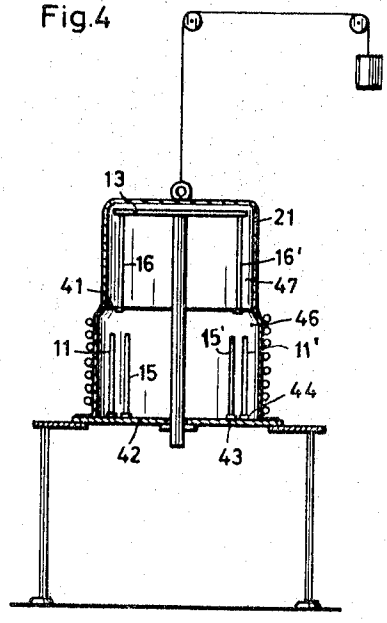


Fig.4



APPARATUS FOR PYROLYTIC PRODUCTION OF SEMICONDUCTOR MATERIAL

Original Filed Nov. 27, 1961 2 Sheets-Sheet 2

Fig.5

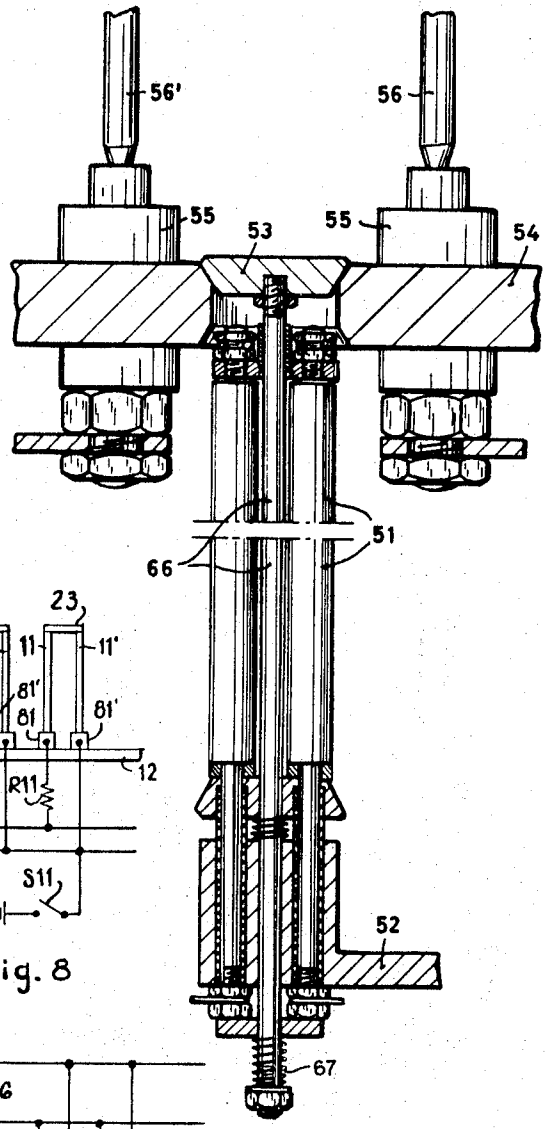


Fig.6

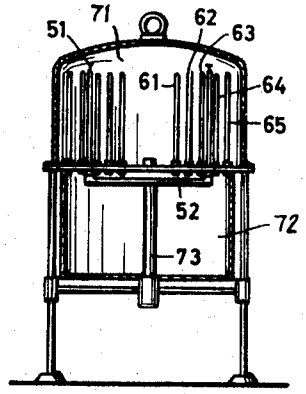


Fig.7

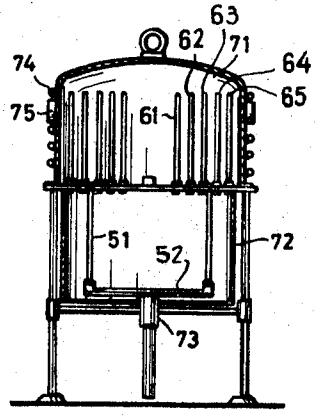


Fig. 8

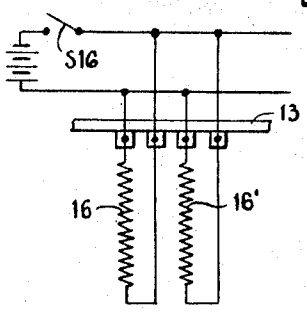


Fig. 9

United States Patent Office 3,342,161
Patented Sept. 19, 1967

3,342,161

APPARATUS FOR PYROLYTIC PRODUCTION OF SEMICONDUCTOR MATERIAL

Max Heim, Munich, Germany, assignor to Siemens Aktiengesellschaft, Berlin, Germany, a corporation of Germany

Original application Nov. 27, 1961, Ser. No. 155,030, now Patent No. 3,240,623, dated Mar. 15, 1966. Divided and this application July 26, 1965, Ser. No. 490,757
5 Claims. (Cl. 118—49.5)

My invention relates to the pyrolytic production of semiconductor material, and has as its general object the improvement of the efficiency and economy of such production by reducing the processing time required and affording, within the same equipment, the simultaneous production of a much larger number of products than heretofore producible in a single operation, and is a division of application Ser. No. 155,030, filed Nov. 27, 1961, now Patent No. 3,240,623.

More particularly, my invention relates to apparatus for the production of semiconductor material, particularly silicon, by thermal dissociation of a gaseous compound of the semiconductor material and precipitation of the semiconductor material onto a multiplicity of carrier or core rods consisting of the same material directly heated by passing electric current through the rods.

The semiconductor rods employed as carriers or cores in pyrolytic production methods, being of extreme purity, have an extremely high specific electric resistance when in cold condition and become appreciably conductive to electric current only at or near incandescent temperatures. Consequently, for maintaining the core rods by direct passage of electric current at the high temperature required for pyrolytic decomposition and precipitation of the semiconductor substance, particularly silicon, it is necessary to first preheat the core rods until they become capable of carrying the electric current required for further maintenance and further increase of their temperature.

According to my invention, the heating, of the cores or carriers, required for reducing the specific electric resistance, prior to commencing the pyrolytic production process proper, is obtained by first filling the reaction vessel, in which the core rods are mounted, with a protective gas of relatively good heat conducting properties, particularly hydrogen, and by placing heater elements as close as feasible to the carrier rods, or at least to a number of those rods accommodated in the processing vessel. By means of these heaters, the core rods, or at least part of them are heated to a temperature sufficient for these rods to assume an electric conductance adequate for maintaining a flow of electric heating current through the rods. Thereafter the heater elements are inactivated or switched-off and are moved out of the reaction chamber into an adjacent space, such as into a container filled with air or protective gas, whereafter the reaction gas, containing the semiconductor compound to be pyrolytically reduced and precipitated, is supplied to the reaction chamber while passing electric current through the rods.

In the production of hyperpure semiconductor material from the gaseous phase, the preheating necessary for reducing the initially high specific resistance of the carrier rods heretofore has been effected with the aid of infrared radiators located outside of the reaction vessel consisting of quartz.

By comparison my invention achieves a number of advantages. In the first place, the transfer of heat from the source to the core or carrier rods is not exclusively due to radiation but is also effected by heat conductance so that the carrier rods can be heated up to the temperature required for good current conductance within a much

shorter period of time than heretofore required. Furthermore, the reaction vessel can be given any desired large size because it is no longer necessary to use a quartz vessel which in practice can be made to a maximum diameter of about 180 mm. Thus, the invention also affords the use of processing vessels consisting of metal and provided with cooling means. In consequence, the invention permits simultaneous precipitation of semiconductor material upon a very large number of carrier rods, for example about 100 rods. In this manner, very large quantities of hyperpure semiconductor material can be produced in a single operation. It has also been found that the economy and efficiency of the pyrolytic production method increases with the number of carrier rods simultaneously employed because the consumption of electric current per carrier is considerably reduced and a better efficiency or yield of the reaction gas being supplied is obtained.

In the apparatus of my invention, it is not necessary to preheat all of the carrier rods by respective heater elements, but it is sufficient to preheat only part of the carrier rods. These heated rods then transfer the heat by radiation or conductance or both to the remaining number of carrier rods, said remaining rods being mounted at a sufficiently small spacing from the initially heated carriers, so that said remaining carrier rods are brought to the temperature required for sufficiently good electric conductance.

For further description, reference will be made in the following to preferred embodiments of apparatus according to the invention illustrated by way of example on the accompanying drawings, in which:

FIGS. 1, 2 and 3 illustrate a first embodiment of a pyrolytic processing apparatus in three different stages of operation respectively.

FIG. 4 illustrates in veritcal section another modification of such apparatus.

FIG. 5 shows partly in section a portion of a further embodiment of such apparatus.

FIGS. 6 and 7 are schematic sectional views of an embodiment of pyrolytic production apparatus in two different stages of operation respectively and utilizing the portion shown in FIG. 5.

FIG. 8 illustrates two pairs of rods together with their electrical connections; and

FIG. 9 schematically shows some of the heater elements with their electrical connections.

The same reference numerals used in the different figures are used to denote the same feature. The apparatus shown in FIGS. 1 to 3 comprises a table structure with a horizontal supporting ring **12**. When preparing the apparatus for pyrolytic production of silicon, a bell-shaped hood portion **21** is lifted off the table structure to make the top surface of the supporting ring **12** accessible. Then the rod-shaped carriers of semiconductor material such as hyperpure silicon are mounted on the ring structure so as to form a peripheral row. Two of these carrier rods are denoted by **11** and **11'** in FIG. 1. The rods are secured at their lower rod end only to respective holders on the ring structure **12** and extend in vertical upright positions. The holders, into which the lower ends of the rods are inserted, insulate these rods from the carrier structure **12**. The rods are spaced from each other a small distance only in the peripheral direction and each two or more of them are connected at the top by an electrically conducting bridge piece of the same hyperpure semiconductor material. This is shown in greater detail in FIG. 8 for two pairs of mutually adjacent carrier rods **11** and **11'** mounted in respective insulated holders **81** and **81'** on the supporting ring **12** and connected at their top ends by bridge pieces **23**. During pyrolytic operation of the

apparatus the reaction chamber, located within the hood **21** is tightly closed by a cover **13** which is mounted on a ported guide rod **14** and thereby displaceable in the vertical direction. Mounted on the bottom side of the cover **13** and downwardly suspended therefrom are electric heating elements in a concentric annular arrangement. Two of these heating elements are shown in FIG. 1 and denoted by **16** and **16'**. Each heating element may consist of a rod-shaped heating resistor as used in electric furnaces. That is, each of the resistance elements **16, 16'** is insulated from the cover plate **13** and connected in an electric heating circuit (FIG. 9) which, when energized by closing switch S16, causes the heating element to be heated to incandescent temperature. Each heating element may also be formed by a heater winding embedded in a metal pipe, such tubular electric heaters being of the kind used for example in conventional hot plates, stoves and baking ovens. If desired, the upper side of the cover **13** may be equipped with another concentric ring arrangement of semiconductor carrier rods of which two are shown in FIG. 1 and denoted by **15** and **15'**, these rods consisting of the same hyperpure material, such as silicon as in the rods **11, 11'**, to constitute respective cores for the pyrolytic precipitation process.

During pyrolytic precipitation, the heater elements **16, 16'** are lowered into a cup-shaped tank **17** which is gas-tightly joined at its rim with the carrier ring **12**. The ring **12** and the cover **13** are preferably provided with respective cooling devices such as tubular coils traversed by cooling water (not shown). A gasket or sealing ring is located at **18** between the supporting ring **12** and the cover **13** so that during pyrolytic operation, with the cover **13** in the position shown in FIG. 1, a hermetic closure of the reaction space within the hood **21** relative to the interior of the tank **17** is secured.

After inserting the core rods and the heating elements into the ring **12** and the cover **13**, the hood **21** is lowered onto the carrier ring **12**, and the reaction chamber now enclosed within the hood **21** is filled with a protective gas, for example hydrogen. The protective gas can be introduced through fitting **14***a* to the hollow guide rod **14** and thence against baffle plate **13'** which distributes the gas over the rods in the reaction space. The reaction gas can also be introduced in the same manner. The hood **21** is provided with a cooling coil **22** for maintaining it at relatively low temperature during pyrolytic precipitation. The residual waste gases are withdrawn through connection **21***a*.

At the commencement of the manufacturing process, the guide **14** is shifted to the position shown in FIG. 2. The tank **17**, by means of connection **17***a*, is preferably filled with the same gas that is also contained in the reaction chamber proper. The peripheral row of heater elements **16, 16'** is now located close to the outer row of the silicon core rods. Now, the heater elements which are provided with the necessary current supply leads (shown in FIG. 9) are electrically heated. The core rods are then heated substantially along their entire length by heat radiation and also by heat conductance since the surrounding gas is of good heat conductance and consists, for example, of hydrogen.

As mentioned, the core rods are likewise provided with current supply leads which are connected for example to the rod holders **81** and **81'** of each two adjacent rods **11, 11'** as shown in FIG. 8, thus being connected through resistors **R11** with a voltage source when switch **S11** is closed. When during the heating-up performance the core rods have assumed such a high temperature that the current passing through the core rod assumes a value sufficient for heating the core rod up to a higher temperature without additional heat from the heater elements, the heater elements are switched-off and the cover **13** on guide rod **14** is lowered to the position shown in FIG. 3 so that the reaction chamber **32** within hood **21** is hermetically separated from the space in tank **17** as apparent from FIG. 3. If the cover **13** is further equipped on its upper side with additional core rods **15, 15'** in an annular arrangement concentric to that of the outer core rods **11, 11'**, then the inner row of core rods **15, 15'** now also becomes electrically conductive due to heat transfer from the outer core rods **11, 11'** and assumes the same incandescent temperature as the rods in the outer row.

Thereafter, the gaseous semiconductor compound to be decomposed and precipitated, for example silico-chloroform, is supplied to the reaction chamber **32**, preferably together with hydrogen and under the influence of the high temperature of the silicon core rods, which are preferably between 1,000 and 1,200° C., and is dissociated with formation of silicon which precipitates onto the carrier rods, thus thickening their diameter. When using monocrystalline core rods, thick rod-shaped monocrystals can be grown in this manner.

In the modified apparatus according to FIG. 4, the above-described tank **17** is eliminated. The ring-shaped arrangement of heating elements is suspended from a plate **13**. The hood **21** carries a massive partitioning wall **41** which, when the plate **13** is raised to the illustrated top position, provides, with the aid of the peripheral gasket (not shown), for a hermetic seal between the reaction chamber **46** and the upper space **47** in which then the heater elements **16, 16'** are located. The core rods **11, 15'** are mounted on a supporting plate **42** in two concentric ring arrangements of holders **43** and **44**. For starting the pyrolytic operation by preheating the core rods, the cover plate **13** with the suspended heater elements **16. 16'** is lowered so that the rod-shaped heater elements are located between the two concentric annular rows of core rods and both rows are simultaneously heated to the temperature required for good conductance of the electric current. Thereafter, the plate **13** with the heater elements is lifted to the position shown in FIG. 4 and the pyrolytic operation proper is commenced.

FIG. 5 shows an enlarged portion of another apparatus for performing the method. The complete apparatus embodying FIG. 5 is being described hereinbelow with reference to FIGS. 6 and 7. The enlarged portion according to FIG. 5 serves to provide for a hermetic seal of the reaction chamber by closure means connected with the heater elements. Several rod-shaped heater elements are grouped in parallel to a cluster **51** and fastened in a holder ring **52**. A valve cone **53** is mounted on a rod **66** which coaxially traverses the cluster of heater elements and is provided with spring means **67** tending to hold the disc **53** in closing position. When the holder ring **52** is lowered to the position shown, the valve cone **53** closes a conical bore in a carrier plate **54** on which the holders **55** for the core rods are mounted, of which two are shown in FIG. 5 and denoted by **56** and **56'**.

FIG. 6 shows a processing apparatus provided with closure means according to FIG. 5. The apparatus is shown to comprise five concentric annular rows of semiconductor core rods denoted by **61** to **65** respectively. The holder ring **52** is shifted to raised position and the clusters of heater elements mounted thereon are located between the annular rows **63** and **64** to simultaneously heat both rows. After the core rods in these rows become conductive for sustaining and continuing the heating by means only of the electric current passing through these rods, the carrier ring **52** is lowered and the ceiling of the reaction chamber **71** then takes place by the means and in the manner described above with reference to FIG. 5. It is preferable to provide the apparatus with a tank **72** in order to provide a seal for the guide **73** of the carrier plate **52** and also for preventing the ingress of air or other gas during lowering of the heater elements and for preventing the influx of air in the event of leakage at the closure valves **53**.

FIG. 7 shows the apparatus of FIG. 6 with the carrier ring **22** in lowered position. Due to heat transfer from the incadescent rows **63** and **64** to the inner rows **61, 62**

and the outer row 65, all core rods become heated to the temperature necessary for good current conductance. Thereafter, the reaction gas mixture is introduced into the reaction chamber 71 by suitable means (not shown) similar to that of FIGS. 1 to 3. For measuring the core-rod temperature during pyrolytic precipitation, the water-cooled bell 74 of the apparatus is provided with observation windows 75.

While reference is made in the foregoing to the pyrolytic production of silicon, the method and apparatus according to the invention is also applicable for the production of other semiconductor material, for example, germanium. In this case, the carrier rods also consist of germanium and the gaseous mixture to be dissociated consists essentially of a gaseous germanium compound, particularly a germanium halogenide such as germanium chloroform.

Upon a study of this disclosure, it will be obvious to those skilled in the art that with respect to various details in performance and equipment, my invention permits of various modifications and hence can be given embodiments other than particularly illustrated and described herein, without departing from the essential features of my invention and within the scope of the claims annexed hereto.

I claim:

1. Apparatus for producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto core rods of the same material, comprising a closed vessel structure having an enclosed processing chamber and including an adjacent space within said closed vessel, supporting structure having holder means in said chamber for mounting a multiplicity of core rods parallel and adjacent to each other, conductor means for applying voltage to drive heating current through the rods when preheated; a carrier structure displaceable between active and inactive positions, heater elements mounted on said carrier structure and located close to and along at least some of the core rods when said carrier structure is in said active position for then preheating said rods to electric conductance temperature, means to inactivate and means to move said heater elements to said adjacent space, sealing means closing said processing chamber from said space when said carrier structure is in said inactive position, and duct means connected with said vessel structure for supplying said chamber with non-reactive gas during preheating and with reaction gas during pyrolytic processing.

2. In apparatus according to claim 1, said rod-holder means being arranged in a plurality of concentric annular rows for accommodating corresponding concentric rows of parallel core rods, and said heater elements forming a single annular row concentrically located between said two rows of holder means.

3. Apparatus for producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto core rods of the same material, comprising a closed vessel structure having an enclosed processing chamber and a coaxially and vertically adjacent space, a ring-shaped group of holder means coaxially mounted in said chamber for vertically mounting a multiplicity of respective core rods parallel and adjacent to each other, conductor means for applying voltage to drive heating current through the rods when preheated; a carrier structure axially displaceable in said vessel structure between an active and an inactive position, a ring-shaped group of rod-shaped heater elements mounted on said carrier structure and extending close to and along at least some of the core rods when said carrier structure is in said active position, for then preheating said rods to electric conductance temperature; means for axially displacing said carrier structure to said inactive position after preheating, said heater elements being located in said space when said carrier structure is in said inactive position, sealing means for separating said chamber from said space when said carrier structure is in said inactive position.

4. Apparatus for producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto core rods of the same material, comprising a substantially horizontal support having an opening, a substantially bell-shaped hood extending upwardly from said support above said opening, a cup-shaped tank suspended from said support below said opening in coaxial relation to said hood, a number of rod holders mounted on top of said support and forming an annular group around said opening for vertically mounting the core rods on said respective holders to extend upwardly into said hood, a substantially horizontal carrier vertically movable in said hood and having a lower position near said opening and an upper position, said carrier forming a cover on said opening and separating the space in said tank from the space in said hood when in said lower position, a group of electric heater elements suspended from said carrier and forming an annular group extending close and along said group of core rods for preheating the latter when said carrier is in said upper position, said heater elements being located in said tank when said carrier is in said lower position.

5. Apparatus for producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto core rods of the same material, a closed system comprising a horizontal supporting plate, a bellshaped hood structure seated on said plate and forming therewith a sealed pyrolytic processing chamber, a multiplicity of core-rod holders mounted on said plate beneath said hood structure for vertically mounting respective core rods in said chamber, electric current supply means connected with said holders for heating the rods by passing current therethrough after preheating of the rods, said plate having openings beside at least some of said holders, a carrier vertically movable beneath said plate between a lower and an upper position, vertically elongated electric heater elements vertically mounted on said carrier below said respective openings to pass through said openings into said processing chamber alongside the core rods when said carrier is lifted to said upper position for there preheating the rods, and valve members engageable with said respective openings for sealing them when said carrier is moved to said lower position to seal said processing chamber from said heater elements during pyrolytic processing.

No references cited.

MORRIS KAPLAN, *Primary Examiner.*