METHOD FOR PYROLYTIC PRODUCTION OF SEMICONDUCTOR MATERIAL

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My invention relates to a method and 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 incipient 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 conduction 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 allows 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 method according to 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 conduction 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 conduction.

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 vertical 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 at 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
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. 4. 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 electrical heating circuit (FIG. 9) which, when energized by closing switch S16, causes the heating elements to be heated to incandescent temperature. Each heating element may also be formed by a heating 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 14a to the hollow guide rod 14 and thereby 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 24a.

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 17a, 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 conduction 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 resistor 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 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 heated to 1,500°C, and is discharged 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 FIGGS. 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 pivoted with spring means 67 tending to hold the disc 53 in closing position. When the hood 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 incandescent 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. The method of producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto a multiplicity of core rods of the same material heated by electric current passing through the rods, which comprises the steps of:
   (a) filling the reaction space, prior to introduction of the gaseous semiconductor compound, with a heat-conducting non-oxidizing gas when the rods are still in cold condition, and placing heater elements close to at least part of the rods;
   (b) heating the rods by means of said heater elements to a temperature at which the heated rods have sufficient electric conductance to be thereafter heated by passage of electric current through the rods;
   (c) then discontinuing the heating by said heater elements and moving the elements out of the reaction space;
   (d) and thereafter admitting the gaseous compound of the semiconductor material to the reaction space and performing the pyrolytic production.

2. The method of producing silicon by pyrolytic precipitation from a reaction gas, containing a silicon halogen compound and hydrogen, onto silicon rods heated by electric current passing through the rods, which comprises the steps of:
   (a) filling the reaction space, prior to introduction of the gaseous semiconductor compound, with a heat-conducting non-oxidizing gas when the rods are still in cold condition, and placing separate electric heater elements in proximity and substantially along the entire length of at least part of the rods;
   (b) heating the rods by means of said heater elements to a temperature at which the heated rods have sufficient electric conductance to be thereafter heated by passage of electric current through the rods;
   (c) then discontinuing the heating by said heater elements and moving the elements out of the reaction space into a gas-filled adjacent space;
   (d) and thereafter passing the reaction gas into the reaction space and performing the pyrolytic production.

3. The method of producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto a multiplicity of core rods of the same material heated by electric current passing through the rods, which comprises the steps of:
   (a) filling the reaction space, prior to introduction of the gaseous semiconductor compound, with a heat-conducting non-oxidizing gas when the rods are still in cold condition, and placing heater elements close to at least part of the rods;
   (b) applying to all rods an electric voltage sufficient to subsequently maintain the rods at pyrolytic temperature by electric current driven by said voltage through said rod once the rods are at an incandescent temperature;
   (c) electrically operating said heater elements to thereby first heat some of said semiconductor rods to said incandescent temperature and thereafter permit said first heated rods to also heat all other rods to said temperature;
   (d) then discontinuing the heating by said heater elements and moving them out of the reaction space while continuing the heating of all rods by said current;
   (e) and thereafter admitting the gaseous compound of the semiconductor material to the reaction space and performing the pyrolytic production.

The method of producing semiconductor material by pyrolytic reduction and precipitation of the material from a gaseous compound thereof onto a multiplicity of core rods of the same material heated by electric current passing through the rods, which comprises the steps of:

References Cited by the Examiner

UNITED STATES PATENTS

2,196,767 4/1940 Hasche ................. 23—277
3,010,797 11/1961 Aries ................. 23—223.5
3,011,877 12/1961 Schweikert et al. .... 23—284
3,023,087 2/1962 Enk et al. ............. 23—223.5
3,140,922 7/1964 Sterling ............... 23—223.5
3,147,141 9/1964 Ishizuka ............... 23—277 X

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