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(54) MANUFACTURE OF ELEMENTAL SEMICONDUCTOR MATERIAL

(71) We, WACKER-CHEMITRONIC, GESELLSCHAFT FÜR ELEKTRONIK-GRUNDSTOFFE MBH., a body corporate organised according to the laws of the Federal Republic of Germany, of 8263 Burghausen, Johannes-Hess-Strasse 24, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a process for the manufacture of an elemental semiconductor material, especially silicon, by deposition from the gaseous phase.

Elemental silicon may be manufactured by deposition from a deposition gas comprising a volatile silicon compound, such as a silicon-hydrogen compound or a silicon-halogen compound, and, preferably, a carrier gas, such as hydrogen, onto a substrate, such as thin rods or filaments of silicon, heated to a temperature not less than the temperature at which the volatile silicon compound decomposes under the prevailing conditions to form silicon. The resulting polycrystalline silicon rods may be converted into monocrystalline rods by, for example, a crucible-free zone melting process or may be comminuted and melted for use in, for example a crystal-pulling process or for casting into shaped silicon bodies.

A major disadvantage of this method of manufacturing silicon is that the deposition rate achieved is initially very low because of the initially low surface area of the substrate. The surface area increases as silicon is deposited and hence the deposition rate increases throughout the process, but the low initial rate makes this process uneconomical especially when the polycrystalline silicon is not needed in the form of a rod, such as when it is subsequently to be melted.

Polycrystalline silicon that is subsequently to be melted can be manufactured more economically be deposition from the gaseous phase onto silicon granules in a fluidised bed (*cf.* GB 926 362, US 3 012 861 and US 3 012 862). The silicon granules grow in size as silicon is deposited thereon and, on reaching a certain size, fall out of the fluidised bed. The resulting silicon granulate may then be melted and processed further.

When silicon is desired in molten form, however, it can be more economic to manufacture the silicon directly as molten silicon, thus saving the energy that would be required for melting the silicon were it manufactured in solid form. To this end, DE 25 33 455 A describes a process in which silicon is deposited from the gaseous phase onto quartz rods maintained at a temperature above the melting point of silicon. Molten silicon flows down the rods and is collected. A disadvantage of this process is that, at the high temperatures used, the silicon reacts with the quartz rods to form volatile silicon monoxide, with the result that the rods literally volatilise and have a very short life.

The present invention provides a process for the manufacture of an elemental semiconductor material in molten form by deposition in a melt of the said elemental material and from a deposition gas comprising a volatile compound of the said elemental material, wherein the melt is situated immediately above a sieve floor containing pores having a width within the range of from 0.2 to 2 mm and is maintained at a temperature not less than the temperature at which the said volatile compound decomposes under the prevailing conditions to form the said elemental material and not more than 200 deg C above the melting point of the said elemental material, and wherein the deposition gas is introduced into the melt through the sieve floor under a pressure within the range of from 0.01 to 30 bar.

The process according to the invention is especially suitable for the manufacture of molten silicon, but may also be used for the manufacture of other elemental semiconductor materials in molten form, for example germanium.

When molten silicon is required, the process according to the invention has the advantage over the above-mentioned processes for the manufacture of solid silicon that the need subsequentiy to melt the silicon is eliminated. It also has the advantage over the above-mentioned process for the manufacture of molten silicon that it does not use and consume quartz rods.

The process according to the invention may be carried out in a reactor, for example, of quartz surrounded by carbon, of silicon nitride or, preferably, of glassy carbon. (Glassy carbon is a glass-like carbon, which may be produced by carbonising a spatially cross-linked synthetic resin, and which has a high annealing temperature, preferably of more than 1500°C for the present purpose.) The reactor may suitably be vertically tubular.

In use, the reactor contains a melt of the semiconductor material being manufactured, and this melt is situated immediately above a sieve floor contained within the reactor. The deposition gas is passed through the sieve floor from below, as discussed below. The sieve floor may consist of a quartz frit or, preferably, of glassy carbon. The size of the pores in the sieve floor is not generally critical as regards the semiconductor melt since, for example, liquid silicon has a high surface tension. The pore width should, however, be within the range of from 0.2 to 2 mm, depending partly on the flow velocity of the deposition gas.

At the commencement of the process, the melt may be formed from granules of the elemental material introduced into the reactor through a suitably arranged nozzle at the top of the reactor. These may then be melted under an inert gas atmosphere, for example, by means of a resistance heater arranged around the reactor, by means of a high-frequency heater external of the reactor, or the reactor may contain a heating finger extending into the semiconductor melt.

A deposition gas comprising a volatile compound of the elemental semiconductor material being manufactured is introduced into the melt from below, through the sieve floor. When the elemental semiconductor material being manufactured is silicon, the said compound may be silicon-hydrogen compound or a silicon-halogen compound, for example silane, monochlorosilane, dichlorosilane, tetrachlorosilane, hexachlorodisilane or, preferably, trichlorosilane, Likewise, when the elemental semiconductor material is germanium, the said volatile compound may be a germanium-hydrogen compound or a germanium-halogen compound, for example germanium tetrahydride, germanium monohydride trichloride or germanium tetrachloride. The deposition gas preferably also comprises a carrier gas, for example a noble gas, *e.g.* argon or helium, or, preferably, hydrogen.

Immediately prior to introduction into the melt, the deposition gas is advantageously at room temperature, but, in any case, should be maintained at a temperature below the temperature at which the said volatile compound decomposes under the prevailing conditions to form the respective elemental material, since otherwise the inlet and pipes may become blocked as a result of the deposition therein of the elemental material. For example, when using trichlorosilane as the said volatile compound, the deposition gas should be maintained at a temperature not exceeding 500°C prior to introduction into the melt.

The deposition gas may suitably be introduced into the reactor through a nozzle arranged below the sieve floor, which nozzle is preferably protected from any external heating device arranged around the reactor in order that it remains sufficiently cool that no deposition occurs inside it.

The deposition gas is introduced into the melt under a pressure within the range of from 0.01 to 30 bar, but the said pressure must, of course, be greater than the sum of the hydrostatic pressure of the melt and the pressure of any gas above the melt.

The melt is maintained at a temperature not less than the temperature at which the said volatile compound decomposes under the prevailing conditions to form the respective elemental material and not more than 200 deg C above the melting point of the elemental material. In most cases, the said decomposition temperature is lower than the melting point of the elemental material, in which case it is merely necessary to maintain the elemental material at a temperature not less than its melting point and not more than 200 deg C thereabove. In the case of a silicon melt, the melt should be maintained at a temperature within the range of from 1410°C (the melting point of silicon) to 1610°C, preferably from 1420 to 1470°C, and in the case of a germanium melt, the melt should be maintained at a temperature within the range of from 937°C (the melting point of germanium) to 1137°C, preferably from 940 to 970°C.

As the deposition gas passes into and through the melt, the said volatile compound decomposes to form the respective elemental material, which is deposited in molten form in the melt. Additional melt is thus manufactured as the deposition gas passes through it, and may be withdrawn from the reactor either continuously or discontinuously.

To this end, the reactor may be provided with an over-flow outlet for the semiconductor melt, so arranged as to maintain a constant liquid level within the reactor. This outlet, or an additional outlet, may be arranged as a siphon such that semiconductor melt may be forced out through the outlet by exerting gas pressure on the melt surface within the reactor. The reactor may additionally or alternatively contain an outlet, provided with a stop-cock, immediately above the sieve plate, through which melt may be removed from the reactor as desired.

The reactor preferably contains a chamber arranged below the sieve floor to collect any semiconductor melt that passes through the sieve floor and also any that is formed as a result of the volatile compound decomposing on contacting the hot sieve floor. This chamber may also be provided with an outlet for the discontinuous removal of the melt therefrom, the outlet having a suitable safety cock, for example a valve, stop-cock or gas counter-pressure arrangement. Alternatively, the outlet may be arranged for the continuous removal of a melt from the said chamber.

The semiconductor melt removed from the reactor may be used directly for casting into plates, bars, rods or other shaped articles.

Residual gases (that is unreacted volatile compound and carrier gas) and waste gases (that is gases formed as a result of the decomposition of the folatile compound) issue from the melt. They may subsequently be removed from the reactor, in which case, they are first advantageously cooled to a temperature below the said decomposition temperature of the volatile compound in order to prevent deposition of the elemental material within the pipes by which these gases leave the reactor. Such cooling may be effected by passing a gaseous coolant, for example hydrogen, helium or argon, into the gas space above the melt suitably at a temperature within the range of from 20 to 50°C. This gaseous coolant can then leave the reactor together with the residual and waste gases. Any unreacted volatile compound can be separated from this gas mixture by condensation and be recirculated. Alternatively, the reactor may contain a plurality of semi-conductor melts arranged one above another, and each separated from the melt immediately below it by means of a sieve floor and a gas space, such that the residual and waste gases from the (first) lowermost melt pass through the other melts in succession, in which case unreacted volatile compound issuing from the first melt may be consumed in the second and subsequent melts and the residual and waste gases finally issuing from the reactor may contain very little or no unreacted volatile compound.

One method of carrying out the process according to the invention for the manufacture of silicon will now be described, by way of example only, with reference to the accompanying drawing, which shows a diagrammatic vertically cross-sectional representation of a reactor suitable for carrying out the process according to the invention.

Silicon granules are introduced into a vertically tubular reactor 1, which is of glass carbon having a glow temperature of more than 1500°C, by means of an inlet 2, such that they lie on a sieve floor 3, which is also a glassy carbon having an annealing temperature of more than 1500°C and which contains pores having a diameter within the range of from 0.2 to 2 mm. The granules are then heated, under an inert gas atmosphere, by means of a resistance heater 4 arranged around the reactor, to form a silicon melt 6, which is maintained at a temperature within the range of from 1420 to 1470°C.

A deposition gas consisting of a volatile decomposable silicon compound and a carrier gas is introduced into the reactor, under a pressure within the range of from 0.01 to 30 bar, through a nozzle 5, which is situated below the sieve floor 3 and is provided with a heat insulation jacket 7 to prevent the nozzle 5 from being heated to a temperature above about 500°C by means of the resistance heater 4. The deposition gas passes through the sieve floor 3 and into the silicon melt 6, through which it passes in the form of a large number of small gas bubbles. As the deposition gas passes through the melt, it is heated to such a temperature that the volatile silicon compound decomposes and forms additional molten silicon. As additional molten silicon is formed, silicon melt flows out of a siphon/overflow outlet 8 such that the level of the silicon melt 6 within the reactor 1 is maintained constant at the level shown in the drawing. If additional silicon melt is temporarily required from the reactor 1, the level of the silicon melt 6 within the reactor 1 may be forced below the level shown to the level at which the outlet 8 leaves the reactor by exerting gas pressure on the surface of the silicon melt 6, for example by closing the gas outlet 14 (mentioned below). The reactor 1 is also provided with an outlet 9 for silicon melt, situated immediately above the sieve floor 3 and provided with a stop-cock. Silicon melt can be run off from the reactor 1 through this outlet 9 as desired and in order to empty the reactor 1.

Some molten silicon is formed as a result of the volatile silicon compound decomposing on contact with the sieve floor 3 and this collects in a chamber 10 below the sieve floor 3 and can be run off continuously or discontinuously through an overflow outlet 11 provided with a stop-cock.

Residual deposition gas and waste gases formed on decomposition of the volatile silicon compound issue from the silicon melt 6 into a gas space 12 thereabove, where they are cooled to a temperature below the decomposition temperature of the volatile silicon compound by means of a gaseous coolant introduced, at a temperature of from 20 to 50°C, through an inlet 13 situated above the silicon melt. The residual, waste and cooling gases then leave the reactor 1 through a gas outlet 14.

The following example was carried out in the manner described above with reference to the drawing in order to illustrate the process of the invention.

The reactor used was made of glassy carbon having an annealing temperature of more than 2500°C and commercially available as "Sigradur D" ("Sigradur" is a Trade Mark); it had a diameter of 60 mm. Silicon granules were introduced into the reactor 1 and heated, under an argon atmosphere, to a temperature of 1430°C to give a silicon melt 6 having a depth of 50 mm. A deposition gas, consisting of trichlorosilane and hydrogen in a molar ratio of 1:1, was introduced into the reactor 1 through the nozzle 5 under a pressure of about 1.6 bar and at a rate of 200 Nl/h. ("Nl" means a "normal litre", that is a litre measured at normal temperature and pressure.) The deposition gas passed through the silicon melt 6 into the gas space 12, into which argon was introduced through the inlet 13 at a temperature of about 25°C and at a rate of 1000 Nl/h. The pressure in the gas space 12 was 1.5 bar. Molten silicon issued from the outlets 8 and 11 at a combined rate of 20 g/h, corresponding to a yield of 0.20 g of silicon per Nl of trichlorosilane.

WHAT WE CLAIM IS:

1. A process for the manufacture of an elemental semi-conductor material in molten form by deposition in a melt of the said elemental material and from a deposition gas comprising a volatile compound of the said elemental material, wherein the melt is situated immediately above a sieve floor containing pores having a width within the range of from 0.2 to 2 mm and is maintained at a temperature not less than the temperature at which the said volatile compound decomposes under the prevailing conditions to form the said elemental material and not more than 200 deg C above the melting point of the said elemental material, and wherein the deposition gas is introduced into the melt through the sieve floor under a pressure within the range of from 0.01 to 30 bar.

2. A process as claimed in claim 1, carried out in a reactor of glassy carbon having an annealing temperature of more than 1500°C.

3. A process as claimed in claim 1 or claim 2, wherein the sieve floor is of glassy carbon having an annelaing temperature of more than 1500°C.

4. A process as claimed in any one of claims 1 to 3, wherein a chamber is arranged below the sieve floor to collect any melt that passes through the sieve floor and any formed as a result of the volatile compound decomposing on contacting the sieve floor.

5. A process as claimed in any one of claims 1 to 4, wherein the deposition gas additionally comprises a carrier gas.

6. A process as claimed in claim 5, wherein the carrier gas is hydrogen.

7. A process as claimed in any one of claims 1 to 6, wherein residual and waste gases issuing from the melt are cooled by means of a gaseous coolant, to a temperature below the said decompositon temperature.

8. A process as claimed in claim 7, wherein the gaseous coolant is hydrogen, helium or argon.

9. A process as claimed in any one of claims 1 to 8, wherein the elemental material is silicon.

10. A process as claimed in claim 9, wherein the melt is maintained at a temperature within the range of from 1420 to 1470°C.

11. A process as claimed in claim 9 or claim 10, wherein the volatile compound is trichlorosilane.

12. A process as claimed in claim 11, wherein, immediately prior to introduction into the melt, the deposition gas is at a temperature not exceeding 500°C.

13. A process as claimed in any one of claims 1 to 12, wherein the elemental material is germanium.

14. A process as claimed in claim 13, wherein the melt is maintained at a temperature within the range of from 940 to 970°.

15. A process as claimed in claim 1, carried out substantially as described herein with reference to the accompanying drawing.

16. A process as claimed in claim 1, carried out substantially as described in the Example herein.

17. An elemental semiconductor material that has been manufactured by a process as claimed in any one of claims 1 to 16.

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1572479 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*