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(54) MANUFACTURE OF SILICON

(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 silicon by deposition from the gaseous phase onto a silicon granulate in a fluidised bed.

Silicon may be manufactured by deposition from a gaseous silicon compound onto a substrate, which may be, for example, a thin silicon rod. Two such rods are usually joined together by means of a bridge and are heated to a deposition temperature of, for example, from 1100 to 1200°C by the passage of an electric current therethrough while situated in a reactor of, for example, quartz through which a deposition gas comprising, for example, trichlorosilane and hydrogen is being passed. The trichlorosilane is decomposed to form, *inter alia,* silicon, which is deposited on the thin rods. Three major disadvantages of this method are, first, that the process is discontinuous, secondly, that the thin rods used have to be manufactured from thicker polycrystalline silicon rods by zone-pulling and, thirdly, that the initial deposition rate is very low and increases only as the surface area of the rod increases as silicon is deposited thereon.

In order to overcome these disadvantages, it has been proposed to deposit silicon from a gaseous silicon compound onto silicon granules in fluidised bed (*cf.* GB 926,362). Heating of the silicon granules in the fluidised bed may be carried out by means of an inductively heated rod within the fluidised bed, by direct heating by means of electrodes within the fluidised bed with the fluidised bed acting as an ohmic resistance, or by continuously circulating the silicon granules through the fluidised bed and through a separater heater. These heating methods involve the use of complicated additional apparatus within the fluidised bed itself and/or involve the continuous circulation of the fluidised bed into and out of the reactor, and thus they increase the complexity of the process. Alternatively, the passage of the gaseous silicon compound into the reactor may be interrupted periodically by introducing into the reactor chlorine, hydrogen chloride or another gas that will react with the decomposition product(s) of the gaseous silicon compound in an exothermic reaction, the introduction of the gaseous silicon compound being resumed when enough heat has been formed to heat the granules to the desired temperature. This method has the obvious disadvantage that it entails the periodic interruption of the process.

It has also been proposed, in order to ensure that the entire fluidised bed of silicon granulate is maintained at the desired deposition temperature, to heat the whole of the interior of the fluidised-bed reactor to the deposition temperature by means of heating coils surrounding the walls of the reactor (*cf.* US 3,012,861 and 3,012,862). This, however has the disadvantageous result that silicon is deposited not only onto the silicon granules but also onto the interior walls of the reactor, onto the seive plate below the silicon granulate and in the gas supply pipes. This process also cannot therefore, in practice, be carried out continuously but has to be terminated periodically in order that the reactor may be cleaned. Moreover, when using a quartz reactor, because of the extremely large difference between the thermal expansion coefficient of the quartz reactor walls and that of the silicon layer deposited thereon, the reactor becomes very susceptible to even slight thermal shock, with the result that the quartz reactor usually breaks during cooling prior to cleaning or may even break

earlier thus prematurely terminating the process.

It has been proposed to overcome this problem of reactor breakage by terminating deposition after a short period of from 30 to 90 minutes, and then cooling the reactor in order to shatter the thin silicon layer deposited on the quartz wall. The reactor may then be reheated, whereafter any further silicon deposited on the reactor walls is said to adhere thereto only lightly and continuously to peel off (*cf.* US 3,963,838). An obvious disadvantage of this process is that the deposition has to be terminated temporarily only a short while after the commencement of the process. In any case, the process does not entirely overcome the problem of deposition of silicon on the reactor walls but merely attempts to lessen the problem.

The present invention provides a process for the manufacture of silicon, which comprises continuously passing a deposition gas comprising a volatile silicon compound through a fluidised bed of silicon granules contain within a fluidised-bed reactor while maintaining the said granules at a deposition temperature not less than the temperature at which the volatile silicon compound decomposes to form silicon under the conditions prevailing within the fluidised bed and while maintaining the walls of the reactor at a temperature below the said decomposition temperature of the volatile silicon compound, wherein a carrier gas is continuously introduced in the reactor separately from the deposition gas in such a manner that the carrier gas and the deposition gas mix in, but not upstream of, the fluidised bed and wherein the respective temperatures of the deposition gas and the carrier gas prior to their mixing are such that neither of the said gases decomposes to form silicon under the conditions prevailing upstream of the region of mixing and are also such that the said gases together maintain the silicon granules at the deposition temperature.

The fluidised-bed reactor used in the process according to the invention may be a conventional fluidised-bed reactor provided with an appropriate number of inlets and outlets for gases and for the silicon granulate. The reactor will normally contain a sieve plate in the bottom thereof, which should advantageously have a mesh size slightly smaller than that of the smallest silicon granules to be used, so that no silicon granules fall through the sieve plate. The reactor may suitably be of carbon, metal or quartz.

During the process of the invention, the walls of the reactor have to be maintained at a temperature below the temperature at which the respective volatile silicon compound decomposes to form silicon under the prevailing conditions (herein referred to as the decomposition temperature). This may be achieved by circulating a coolant through a jacket provided in the reactor walls, but, in many cases, this will not be necessary because the decomposition temperature of the volatile silicon compound is often so high that the walls of the reactor are cooled sufficiently simply by means of the surrounding atmosphere. An inert gaseous coolant, for example argon, may be introduced into the reactor above the fluidised bed in order to assist in cooling this part of the reactor.

The silicon granulate constituting the fluidised bed serves as the substrate for the deposition of silicon and is preferably of high purity. The particle size of the granules is advantageously within the range of from 50 to 2000 μm, preferably from 200 to 500 μm.

The volatile silicon compound used as the deposition gas may be such a compound as is conventionally used for the deposition of silicon from the gaseous phase onto a substrate. Suitable volatile silicon compounds are, for example, silane or a halogenosilane, for example monochlorosilane, dichlorosilane, silicon tetrachloride, hexachlorodisilane or, preferably, trichlorosilane. A mixture of two or more volatile silicon compounds may be used as the deposition gas. During the process according to the invention, the silicon granules have to be maintained at a temperature (the deposition temperature) not less than the decomposition temperature of the respective volatile silicon compound.

The pressure prevailing inside the reactor during the deposition is advantageously within the range of from 0.6 to 30 bar, preferably from 1.5 to 5 bar.

Under such pressures, when using trichlorosilane as the volatile silicon compound, the deposition temperature is advantageously within the range of from 720 to 1250°C, preferably from 800 to 950°C, and, when using dichlorosilane as the volatile silicon compound, the deposition temperature is advantageously within the range of from 350 to 1000°C, preferably from 600 to 900°C. The deposition gas should not, of course, decompose prior to entering the fluidised bed, since otherwise silicon may be deposited on the gas-supply pipe and on the sieve plate, and (except in special circumstances such as when using silicon tetrachloride and hydrogen as discussed below) the deposition gas should reach its decomposition temperature only after entering the fluidised bed.

According to the process of the invention, the heating of the deposition gas to the

desired deposition temperature and/or the maintenance of the deposition gas at the desired deposition temperature is achieved by continuously introducing a carrier gas into the reactor, separately from the deposition gas, in such a manner that the carrier gas and deposition gas mix in, but not upstream of, the fluidised bed. The respective temperatures of the deposition gas and the carrier gas prior to their mixing are such that neither of the said gases decomposes to form silicon under the conditions prevailing upstream of the region of mixing and are also such that the said gases together maintain the silicon granules at the desired deposition temperature.

The carrier gas should be stable at the temperature and under the conditions at which it is introduced into the reactor at least for the duration of the relevant period. It should also, of course, not lead to impurities in the deposited silicon, but it need not necessarily be inert under the deposition conditions: for example it may, in some cases, be a gas such as hydrogen which may react with the volatile silicon compound or it may itself be a volatile silicon compound. Suitable carrier gases are, for example, nitrogen, hydrogen, silicon tetrachloride and noble gases, for example argon. Silicon tetrachloride is preferably used as the carrier gas, both because of its high specific thermal capacity (Cp=0.13 cal/°K.g) and its availability in a very pure form fairly inexpensively.

Two or more carrier gases may be used in addition to the deposition gas, in which case they may be introduced into the reactor either separately or—depending on the particular carrier gases—as a mixture. Argon and hydrogen, may, for example, be introduced into the reactor as a mixture. On the other hand, silicon tetrachloride and hydrogen could not normally be introduced as a mixture because silicon tetrachloride decomposes in the presence of hydrogen at about 1000°C (although in the absence of hydrogen it does not decompose until above 1300°C); silicon tetrachloride and hydrogen could, however, be used simultaneously as carrier gases provided that they are introduced in such a manner that they (and the deposition gas) did not mix upstream of the fluidised bed.

The ratio of the volume of the deposition gas to the volume of the carrier gas is preferably within the range of from 1:1 to 3:4.

The temperature at which the carrier gas is introduced into the reactor depends on a number of factors including the desired deposition temperature, the thermal capacity of the carrier gas, the temperature at which the deposition gas is introduced, the ratio of the amount of the deposition gas to the amount of the carrier gas, the temperature at which the silicon granulate is introduced into the reactor, and the rate of flow of the gases through the reactor. Normally, the carrier gas will be introduced into the reactor at a temperature greater than the desired deposition temperature while the deposition gas will be introduced at a temperature lower than the desired deposition temperature (and, indeed, lower than its decomposition temperature).

When, for example, the deposition gas is trichlorosilane and the carrier gas is silicon tetrachloride, the deposition gas is advantageously introduced at a temperature within the range of from 300 to 600°C, preferably from 500 to 600°C, while the carrier gas is advantageously introduced at a temperature within the range of from 800 to 1300°C, preferably from 1000 to 1100°C, in order to achieve a deposition temperature within the respective range given above. Appropriate temperature ranges for other combinations of gases may readily be ascertained from a consideration of the factors mentioned above.

In certain special cases, when the presence of the carrier gas affects the temperature at which the volatile silicon compound decomposes, the deposition gas may be introduced into the reactor at a temperature greater than the deposition temperature, that is at a temperature greater than the decomposition temperature under the deposition conditions prevailing in the fluidised bed but lower than the decompositon temperature under the conditions under which the deposition gas enters the reactor. For example, when the deposition gas is silicon tetrachloride and the carrier gas is hydrogen, either gas may be the hotter of the two gases, provided that the silicon tetrachloride is introduced into the reactor at a temperature below that at which it decomposes in the absence of hydrogen and that the mixture of the two gases in the fluidised bed is at a temperature greater than that at which silicon tetrachloride decomposes in the presence of hydrogen.

The deposition gas decomposes at the deposition temperature and under the deposition conditions with the result that silicon is deposited on the silicon granules, which thus gradually grow in size until they settle out of the fluidised bed, whereupon they may be sucked off by an outlet pipe. Fresh silicon granules may be continually added to the fluidised bed to replace those removed. They are preferably introduced into the reactor above the level of the fluidised bed and are preferably prewarmed before being introduced.

A small proportion of new silicon particles

are also formed during the deposition, and these then also grow as fresh silicon is deposited on them.

The process according to the invention is carried out in a continuous manner and can achieve deposition rates ten times those achievable when depositiong silicon from the gaseous phase onto thin rods.

The high-purity polycrystalline silicon granules obtained in the present process may be melted, for example, to form moulded articles or to be used as the starting material for the Czochralski crystal-pulling process for the manufacture of a monocrystalline silicon rod.

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

A substantially cylindrical fluidised-bed reactor 2 of quartz, with an internal diameter of 60 mm, contains a sieve plate 4, constituted by a porous quartz frit, and is provided with a jacket 8 through which a coolant can be passed *via* an inlet 9 and an outlet 10. An inlet 1 for silicon granules is provided in the top of the reactor 2 and an outlet 6, through which silicon granules that settle out of the fluidised bed 3 (which is present when the reactor is in use) may be removed, is provided immediately above the sieve plate 4. An inlet 11 for the deposition gas is provided below the sieve plate 4 and an inlet 5 for the carrier gas is provided immediately above the sieve plate 4. An outlet 7 for residual and waste gases is provided in the top of the reactor 2.

High-purity silicon granules having particle sizes within the range of from 400 to 500 μm and prewarmed to a temperature of about 850°C were continuously fed through the inlet 1 into the reactor 2 where they constituted the fluidised bed 3. Equal volumes of trichlorosilane (the deposition gas) at a temperature of 580°C and silicon tetrachloride (the carrier gas) at a temperature of 1100°C were fed into the reactor 2 through the inlets 11 and 5 respectively, at a total rate of 1.5 m^3/h (measured at standard temperature and pressure). The two gases mixed in the fluidised bed and maintained it at a temperature of about 850°C under a pressure of 1.5 bar. Residual and waste gases were removed through the outlet 7. The walls of the reactor 2 were maintained at a temperature below the deposition temperature simply by the cooling effect of the surrounding atmosphere. Silicon was deposited on the granules in the fluidised bed with a yield of 0.28 gram of silicon per litre of gaseous trichlorosilane and at a rate of 210 g Si/h. Silicon granules that settled out of the fluidised bed were removed through the outlet 6.

The process was repeated under identical deposition conditions in a similar reactor having an internal diameter of 200 mm and with a total gas flow of 17 m^3/h (measured at standard temperature and pressure). A deposition rate of 2400 g Si/h was obtained.

WHAT WE CLAIM IS:—

1. A process for the manufacture of silicon, which comprises continuously passing a deposition gas comprising a volatile silicon compound through a fluidised bed of silicon granules contained within a fluidised-bed reactor while maintaining the said granules at a deposition temperature not less than the temperature at which the volatile silicon compound decomposes to form silicon under the conditions prevailing within the fluidised bed and while maintaining the walls of the reactor at a temperature below the said decomposition temperature of the volatile silicon compound, wherein a carrier gas is continuously introduced into the reactor separately from the depositon gas in such a manner that the carrier gas and the deposition gas mix in, but not upstream of, the fluidised bed and wherein the respective temperatures of the deposition gas and the carrier gas prior to their mixing are such that neither of the said gases decomposes to form silicon under the conditions prevailing upstream of the region of mixing and are also such that the said gases together maintain the silicon granules at the deposition temperature.

2. A process as claimed in claim 1, wherein the silicon granules are of a particle size within the range of from 50 to 2000 μm.

3. A process as claimed in claim 2, wherein the silicon granules are of a particle size within the range of from 200 to 500 μm.

4. A process as claimed in any one of claims 1 to 3, wherein the walls of the reactor are maintained at a temperature below the said decomposition temperature by means of the cooling effect of the surrounding atmosphere.

5. A process as claimed in any one of claims 1 to 3, wherein the walls of the reactor are maintained at a temperature below the said decomposition temperature by means of a coolant flowing through a jacket provided in the reactor walls.

6. A process as claimed in any one of claims 1 to 5, wherein the walls of the reactor are maintained at a temperature below the said decomposition temperature by means of an inert gaseous coolant within the reactor above the fluidised bed.

7. A process as claimed in any one of claims 1 to 6, wherein the deposition gas and the carrier gas are used in a respective

volume ratio within the range of from 1:1 to 3:4.

8. A process as claimed in any one of claims 1 to 7, wherein the carrier gas is nitrogen, hydrogen or a noble gas.

9. A process as claimed in any one of claims 1 to 7, wherein the carrier gas is silicon tetrachloride.

10. A process as claimed in any one of claims 1 to 9, wherein the deposition gas comprises a silane or a halogenosilane.

11. A process as claimed in claim 10, wherein the deposition gas comprises trichlorosilane.

12. A process as claimed in claim 10, wherein the deposition gas comprises dichlorosilane.

13. A process as claimed in any one of claims 1 to 12, wherein the pressure prevailing inside the reactor is within the range of from 0.6 to 30 bar.

14. A process as claimed in claim 13, wherein the pressure prevailing inside the reactor is within the range of from 1.5 to 5 bar.

15. A process as claimed in claims 11 and 13, wherein the deposition temperature is within the range of from 720 to 1250°C.

16. A process as claimed in claims 11 and 14, wherein the deposition temperature is within the range of from 800 to 950°C.

17. A process as claimed in claims 12 and 13, wherein the deposition temperature is within the range of from 350 to 1000°C.

18. A process as claimed in claims 12 and 14, wherein the deposition temperature is within the range of from 600 to 900°C.

19. A process as claimed in claims 9 to 15, wherein the trichlorosilane is introduced into the reactor at a temperature within the range of from 300 to 600°C and the silicon tetrachloride is introduced into the reactor at a temperature within the range of from 800 to 1300°C.

20. A process as claimed in claims 9 and 16, wherein the trichlorosilane is introduced into the reactor at a temperature within the range of from 500 to 600°C and the silicon tetrachloride is introduced into the reactor at a temperature within the range of from 1000 to 1100°C.

21. A process as claimed in claims 9 and 17, wherein the dichlorosilane is introduced into the reactor at a temperature within the range of from 200 to 350°C and the silicon tetrachloride is introduced into the reactor at a temperature within the range of from 500 to 1300°C.

22. A process as claimed in claims 9 and 18, wherein the dichlorosilane is introduced into the reactor at a temperature within the range of from 250 to 320°C and the silicon tetrachloride is introduced into the reactor at a temperature within the range of from 1000 to 1100°C.

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

24. Silicon manufactured by a process as claimed in any one of claims 1 to 23.

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1570131 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale