

RESERVE COPY

PATENT SPECIFICATION

Inventors: WILLIS ALFRED ADCOCK and RAYMOND CHARLES SANGSTER.

799,876



Date of Application and filing Complete Specification Nov. 23, 1956.

No. 35943/56.

Complete Specification Published Aug. 13, 1958.

Index at acceptance: —Classes 1(2), E3A; 1(3), A1D10, A1G39D10; and 90, K10.

International Classification: —C01b, g.

COMPLETE SPECIFICATION

Method of Preparing Pure Silicon

5 We, TEXAS INSTRUMENTS INCORPORATED, of 6000, Lemmon Avenue, Dallas, Texas, United States of America, a Corporation organized and existing under the laws of the State of Delaware, United States of America, 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:—

10 This invention relates to a method for the production of highly purified silicon, especially useful in the production of electrical semiconductor devices.

15 The extensive use of silicon in electrical semi-conductor devices has necessitated the production of relatively large quantities of ultra pure silicon. Impurities, even in the amount of one part in ten million, are highly undesirable, and this makes necessary lengthy, tedious and costly purification processes. The common method of reducing silicon tetrachloride (SiCl_4) with zinc yields a product which leaves much to be desired in the way of

25 purity. Ordinarily, this product requires extensive further treatment to remove all traces of zinc and of any other impurities that may be present in either the silicon tetrachloride or the zinc.

30 Silicon tetrachloride can be reduced with hydrogen to yield very high purity silicon. However, even at a temperature of 1150°C ., and using a silicon tetrachloride to hydrogen ratio of 0.0685, only 12 per cent. of the silicon tetrachloride is converted to silicon. As a

35 result, only 1.6 per cent. of the available hydrogen is used, and a pound of silicon requires the use of 1636 cubic feet of hydrogen and 50.4 pounds of silicon tetrachloride. In addition to the cost of these initial materials, there is a serious problem of purifying the materials to begin with in order that appreciable quantities of impurities will not carry over the silicon product.

[Price 3s. 6d.]

45 The object of the present invention is to provide a process in which ordinary reagent quality silicon tetrachloride may be converted into ultra high purity silicon, efficiently, and by the use of other chemicals of ordinary reagent quality.

50 According to the present invention there is provided a method of converting silicon tetrachloride into highly purified silicon that comprises passing a mixture of silicon tetrachloride and hydrogen into a high temperature zone maintained at a temperature sufficient to cause substantial reaction to take place, with the formation of silicon and hydrogen chloride, allowing the silicon to deposit in said zone, removing from the zone the unreacted silicon tetrachloride and hydrogen together with the hydrogen chloride formed by the reaction, adding additional silicon tetrachloride and hydrogen to the removed mixture to make up for that used in the reaction and selectively removing from the mixture the hydrogen chloride formed in the reaction, and recirculating the resultant mixture through the reaction zone.

55 The high temperature reaction zone may be maintained at a temperature of 1100 — 1300°C ., preferably 1200°C .

60 The removal of hydrogen chloride and addition of hydrogen may be effected simultaneously by the introduction of vapourised zinc into the system so as to react with the hydrogen chloride to form hydrogen and zinc chloride, and removal of the zinc chloride. The reaction with the zinc chloride may be carried out at a temperature of 600 — 800°C ., preferably 650°C . The zinc chloride may be removed by passing the mixture of hydrogen, hydrogen chloride and silicon tetrachloride first through a cooling and settling chamber and then through a gas filter, e.g. of glass wool. The introduction of the vapourised zinc is preferably effected after the addition of make-up silicon tetrachloride.

65 The reaction of the invention is incomplete

but that fact does not make the over-all process incomplete, because silicon tetrachloride is subsequently added to the mixture flowing out of the reaction zone so as to make up for that decomposed in the reaction zone, the hydrogen chloride is removed and make-up hydrogen added or formed in the mixture, and the mixture is recycled to the reaction zone. By using zinc vapour to split the hydrogen chloride in the effluent from the reaction zone, and thus to reconstitute the hydrogen in the mixture and form zinc chloride as a by product, it is possible to perform a purification step at the same time that the mixture is being brought back to its proper proportions of silicon tetrachloride and hydrogen. The formation of the zinc chloride and its subsequent removal by settling, and filtration through some material such as glass wool, tends also to remove incidental impurities from the mixture, and thus avoid contamination of the final product. The unused silicon tetrachloride and hydrogen being recycled add no new impurities, and this tends to simplify the matter of keeping the system uncontaminated.

Further details and advantages of this invention will be apparent from the appended drawings and the following detailed description of the preferred embodiment of the process of the invention, as illustrated therein.

In the accompanying drawings:—

Figure 1 is a flow diagram in bare outline of an integrated three step process comprising the purification of the silicon tetrachloride, the production of the silicon, and recovery of the silicon produced;

Figure 2 is a diagrammatic illustration of the adsorption step;

Figure 3 is a flow diagram of the silicon production step; and

Figure 4 is a diagrammatic illustration of an apparatus for accomplishing the silicon production step, certain parts being cut away to more clearly show the working elements.

As illustrated in Figure 1, silicon tetrachloride, generally of reagent quality, although not ultra purified at this point in the process, is fed first into an adsorption apparatus, which purifies the silicon tetrachloride and removes such impurities therefrom as might later be detrimental to the process. From this adsorption step, the silicon tetrachloride passes to a fractionating column where it is separated from solvent and residual impurities and then to a cyclic silicon deposition step, to which zinc metal also is introduced, and in this part of the process, the silicon is separated from the silicon tetrachloride and deposited in a highly purified form, usually in a quartz or silicon dioxide tube. From this part of the process, zinc chloride results as a byproduct and highly purified silicon is removed, usually encased in the quartz or silicon dioxide tube, in which it was deposited. In the final step of the process, the quartz tube is removed from the silicon, and

the silicon is melted down under conditions carefully controlled to prevent contamination, and formed into ingots or other suitable form for further use.

The adsorption process is preferably performed in apparatus of the type shown in Figure 2. This apparatus may be of quartz to improve the purity of the product, but does not necessarily have to be so. The silicon tetrachloride is placed in the reservoir 10 of a separatory funnel and passes downwardly through a stopcock 11 of this funnel and into a receiver 12, positioned therebelow. A fitting 13 between the stopcock 11 and the receiver 12 provides an entrance for solvent, such as dichloromethane, trichloromonofluoromethane or trichlorotrifluoroethane, which mixes with the silicon tetrachloride in the receiver 12, and the two then pass downwardly through a three-way stopcock 14 into an adsorption column 15, which is filled with activated aluminum oxide, which tends to adsorb the undesired impurities from the silicon tetrachloride.

Silicon tetrachloride has a symmetrical molecule with no electrical dipole moment and with a stable electronic structure which shows little or no tendency to make additional chemical bonds. By contrast, such critical impurities as boron trichloride and phosphorus trichloride have unsymmetrical structures which have appreciable dipole moments, and these compounds have strong tendencies to form additional chemical bonds. Thus such impurities are attracted to and held by the active surfaces of the aluminum oxide while the silicon chloride passes on through. At the lower end of the adsorption column 15, there is located a three-necked flask 16, heated by an electrical heating mantle 17 connected to a suitable source of power (not shown) through leads 18. The flask contains a few chips of quartz to prevent violence in the boiling.

The flask 16 contains the usual thermometer 19 and also a connection to a solvent vapor return tube 20, through which solvent vapors pass upwardly to a pair of water-cooled condensers 21 and 22. The solvent is condensed in these condensers and passes downwardly into the fitting 13, which returns it to the system. Any uncondensable gas passes out through the condenser 21 and a soda-lime acid absorption tube 23. When sufficient recycling of solvent has taken place to purify all of the silicon tetrachloride that the apparatus can conveniently handle in one run, the three-way stopcock 14 is rotated to direct the solvent into a solvent recovery reservoir 24, and most of the solvent is thus removed from the system. Escaping gas passes out of the system through an acid absorption tube connected to the solvent recovery reservoir in a conventional manner. In fact, all of the individual parts of this equipment are in themselves conventional and need not be described in detail.

The silicon tetrachloride that remains in the flask after most of the solvent has been boiled off is transferred to a fractionating column (not shown) and there separated from the remaining solvent and residual impurities. This fractionating column is conventional except that it is preferably of quartz to prevent contamination of the silicon tetrachloride by materials, such as boron and arsenic, that might be leached out of glass if it were used.

The purified silicon tetrachloride is used in the second step of the process as illustrated in Figure 3 and 4. A mixture of silicon tetrachloride, hydrogen and hydrogen chloride continuously emerges from the silicon deposition tube 31. To this is added enough silicon tetrachloride, from a silicon tetrachloride reservoir 30, to make up for that used in the deposition tube. The mixture, now enriched in silicon tetrachloride, passes to the zinc reaction tube 32, where it is mixed with zinc vapours from a zinc boiler 33, which is maintained at a temperature of 900° C. to 1100° C. The zinc reaction tube itself is maintained at a temperature of 600° C. to 800° C. In this reaction tube, the zinc vapours combine with the hydrogen chloride to form zinc chloride and hydrogen. The silicon tetrachloride, zinc chloride and hydrogen then pass on to a cooling and settling chamber 34, in which most of the zinc chloride and other impurities are removed. The remaining silicon tetrachloride and hydrogen pass on to the filter 35. This filter is preferably a glass wool filter, and any residual zinc chloride or other solid impurities are removed here. The silicon tetrachloride and hydrogen pass from the filter 35 to the pump 36 and then back to the silicon deposition tube 31, which is heated to around 1100° C. to around 1300° C., and here a portion of the hydrogen reacts with a portion of the silicon tetrachloride to form hydrogen chloride and elemental silicon, which deposits out on the heated tube. The initial hydrogen charge used in the process, as well as any hydrogen required for make-up purposes, is introduced into the system ahead of the zinc reaction tube 32.

In order that there be no contamination problem and that the tube be such as will stand the necessary temperature, it has been found preferable to use a silica or "Vycor" tube. "Vycor" is Corning 96% Silica Glass No. 7900 and is a Registered Trade Mark. The output of the silicon deposition tube 31 is then mixed with additional silicon tetrachloride, as already pointed out.

The preferred temperature for the deposition tube is 1200° C., for the zinc boiler 1050° C., and for the zinc reaction tube 650° C.

Appropriate analytical equipment 37 may be attached to the tubing connecting the pump 36 and the silicon deposition tube 31, so as to either continuously or intermittently receive and analyze a sample of the gases passing to

the deposition tube, for control purposes. Preferably, an infra-red analysis unit and a thermal conductivity cell are used for this analysis, so that both silicon tetrachloride and residual hydrogen chloride concentration can be determined.

Instead of removing the hydrogen chloride by the use of zinc, and thus forming additional hydrogen at the same time, the hydrogen chloride may be removed by adsorption on alumina or silica gel, zeolites, or in any other known way, and additional hydrogen added to make up for that used in the process. This, however, is not as efficient a way of conducting the process as is the use of zinc to reform the hydrogen, and is hence less preferred.

Referring to Figure 4, it will be seen that the parts are illustrated in diagrammatic form and are shown as encased in a cover 40 which is provided with an opening 41, to which an exhaust fan may be connected so as to carry away any fumes that may escape. The details of the analysis and control panel 42 have not been shown, since they are not a part of this invention and can be varied to suit the occasion.

A typical composition of the gas entering the silicon deposition tube 31 is 10 per cent silicon tetrachloride, approximately 0.05 per cent hydrogen chloride, and the remainder hydrogen. The silicon tetrachloride content of this gas may well vary between 5 and 20 per cent, and preferably, the hydrogen chloride content of this gas is as low as possible. The process, however, will operate satisfactorily with a somewhat higher hydrogen chloride content, for example, up to about 0.5 per cent.

A typical composition for the gases leaving the silicon deposition tube 31 would be 9.5 per cent silicon tetrachloride, approximately 2 per cent hydrogen chloride, and the remainder hydrogen. Again, the percentage of silicon tetrachloride may vary from about 5 to 20 per cent, always being a little lower than the percentage at the input to the silicon deposition tube, by reason of the deposition of silicon therein, and a similar variation in the per cent of hydrogen chloride in the exit gas may be noted.

One of the most important preferred features of this invention is that of feeding the silicon tetrachloride into the system just ahead of the zinc reactor. As a result, the silicon tetrachloride is purified by passage through the hot zinc vapour before it reaches the deposition tube. Impurities tend either to be removed by the zinc, or to be quite resistant to deposition in the silicon chamber. Therefore, the zinc vapour, in addition to its primary function of regenerating the hydrogen, also continuously purifies both the incoming silicon tetrachloride and the recycling gas stream. In experimental runs, both prepurified silicon tetrachloride and raw, undistilled silicon tetrachloride gave very high purity silicon when the silicon was depo-

sited according to this process. Thus, while the prepurification process is highly desirable, the silicon deposition step may be operated alone to produce silicon that is quite satisfactory for many purposes.

Besides the inherent self-purification feature, this system has the advantage of complete consumption of the silicon tetrachloride fed into it, and of requiring very little in the way of gas purification and disposal or recovery facilities.

The silicon is normally deposited on the inside of a quartz tube. In some cases, the silicon has shown a tendency to come loose without breaking the quartz tube, but in most instances, the quartz tube has had to be destroyed in the process, but this presents no particular problem. Some of the quartz often tends to remain with the silicon but this may be leached away with hydrofluoric acid.

WHAT WE CLAIM IS:—

1. A method of converting silicon tetrachloride into highly purified silicon that comprises passing a mixture of silicon tetrachloride and hydrogen into a high temperature zone maintained at a temperature sufficient to cause substantial reaction to take place, with the formation of silicon and hydrogen chloride, allowing the silicon to deposit in said zone, removing from the zone the unreacted silicon tetrachloride and hydrogen together with the hydrogen chloride formed by the reaction, adding additional silicon tetrachloride and hydrogen to the removed mixture to make up for that used in the reaction and selectively removing from the mixture the hydrogen

chloride formed in the reaction, and recirculating the resultant mixture through the reaction zone.

2. A method as defined in Claim 1, in which the reaction zone is maintained at a temperature of 1100° C. to 1300° C.

3. A method as claimed in Claim 1 or 2, wherein the removal of hydrogen chloride and addition of hydrogen are effected simultaneously by the introduction of vapourised zinc into the system so as to react with the hydrogen chloride to form hydrogen and zinc chloride, and removal of the zinc chloride.

4. A method as claimed in Claim 3, wherein the reaction with the zinc vapour is carried out at a temperature of 600—800° C.

5. A method as claimed in Claim 3 or 4, wherein the zinc chloride is removed by passing the mixture of hydrogen, hydrogen chloride and silicon tetrachloride first through a cooling and settling chamber and then through a gas filter.

6. A method as claimed in any of Claims 3 to 5, wherein the introduction of vaporised zinc is effected after the addition of make-up silicon tetrachloride.

7. A method of converting silicon tetrachloride into highly purified silicon, which method is substantially as hereinbefore described with reference to the accompanying drawings.

For the Applicants:

F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
29, Southampton Buildings, Chancery Lane,
London, W.C.2.

sited according to this process. Thus, while the prepurification process is highly desirable, the silicon deposition step may be operated alone to produce silicon that is quite satisfactory for many purposes.

5 Besides the inherent self-purification feature, this system has the advantage of complete consumption of the silicon tetrachloride fed into it, and of requiring very little in the way of
10 gas purification and disposal or recovery facilities.

The silicon is normally deposited on the inside of a quartz tube. In some cases, the silicon has shown a tendency to come loose without breaking the quartz tube, but in most
15 instances, the quartz tube has had to be destroyed in the process, but this presents no particular problem. Some of the quartz often tends to remain with the silicon but this may
20 be leached away with hydrofluoric acid.

WHAT WE CLAIM IS:—

1. A method of converting silicon tetrachloride into highly purified silicon that comprises passing a mixture of silicon tetrachloride
25 and hydrogen into a high temperature zone maintained at a temperature sufficient to cause substantial reaction to take place, with the formation of silicon and hydrogen chloride, allowing the silicon to deposit in said zone, removing
30 from the zone the unreacted silicon tetrachloride and hydrogen together with the hydrogen chloride formed by the reaction, adding additional silicon tetrachloride and hydrogen to the removed mixture to make up
35 for that used in the reaction and selectively removing from the mixture the hydrogen

chloride formed in the reaction, and recirculating the resultant mixture through the reaction zone.

2. A method as defined in Claim 1, in which the reaction zone is maintained at a temperature of 1100° C. to 1300° C. 40

3. A method as claimed in Claim 1 or 2, wherein the removal of hydrogen chloride and addition of hydrogen are effected simultaneously by the introduction of vapourised zinc
45 into the system so as to react with the hydrogen chloride to form hydrogen and zinc chloride, and removal of the zinc chloride.

4. A method as claimed in Claim 3, wherein the reaction with the zinc vapour is carried out at a temperature of 600—800° C. 50

5. A method as claimed in Claim 3 or 4, wherein the zinc chloride is removed by passing the mixture of hydrogen, hydrogen chloride and silicon tetrachloride first through
55 a cooling and settling chamber and then through a gas filter.

6. A method as claimed in any of Claims 3 to 5, wherein the introduction of vaporised zinc is effected after the addition of make-up silicon tetrachloride. 60

7. A method of converting silicon tetrachloride into highly purified silicon, which method is substantially as hereinbefore described with reference to the accompanying
65 drawings.

For the Applicants:

F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
29, Southampton Buildings, Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1958
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.

