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A method and a reactor for production of high-purity silicon

The present invention relates to a method and equipment for the production of high purity silicon metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal in the liquid state.

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High purity silicon metal has many applications, of which semiconductor material for the electronic industry and photovoltaic cells for generation of electricity from light are the most important. Presently, high purity silicon is commercially produced by thermal decomposition of high purity gaseous silicon compounds. The most common

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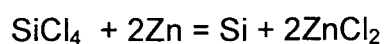
processes use either SiHCl_3 or SiH_4 . These gases are thermally decomposed on hot high purity Si substrates to silicon metal and gaseous by-products.

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The present processes, in particular the thermal decomposition steps, are very energy intensive and industrial production plants are large and expensive. Any new process addressing these issues and at the same time being able to supply Si metal of sufficient purity is therefore highly desirable.

It has long been known that reduction of high purity SiCl_4 with high purity Zn metal has the potential to yield high purity Si metal. In 1949, D.W. Lyon, C.M. Olson and E.D. Lewis, all of DuPont, published an article in J. Electrochem.Soc. (1949, **96**, p.359) describing the preparation of Hyper-Pure Silicon from Zn and SiCl_4 . They reacted gaseous Zn with gaseous SiCl_4 at 950°C , and obtained high purity Si. Later researchers at the Batelle Columbus Laboratories conducted similar tests, but at a much larger scale. Gaseous SiCl_4 and gaseous Zn was fed to a fluidised bed reactor, where Si granules were formed (see e.g. D.A. Seifert and Mf. Browning, AIChE Symposium Series (1982), 78(216), p.104-115). Reduction of SiCl_4 in molten Zn has also been described in various patents. US 4,225,367 describes a process for production of thin films of silicon metal. A gaseous Si-containing species is led into a chamber containing a liquid Zn containing alloy. The gaseous Si-species is reduced on the surface of the alloy and deposits there as a thin Si-film. JP 1997-246853, "Manufacture of high-purity silicon in closed cycle", describes a process for production of high purity silicon. Liquid or gaseous SiCl_4 is reduced with molten Zn to give polycrystalline Si and ZnCl_2 . The ZnCl_2 is separated from the Si by distillation and fed to an electrolytic cell where Zn and Cl_2 are produced. The Zn is used for the reduction of SiCl_4 in a separate reactor, while the chlorine is treated with H to give HCl, which is used to chlorinate metallurgical grade Si. Both Zn and Cl are thus recycled in the process. The obtained Si had a quality suitable for use in solar cells. A similar process is described in WO 2006/100114. A difference between this and JP 1997-246853 is that the melting of the Si resulting from the reduction of SiCl_4 with Zn is to be melted, and thereby purified from Zn and ZnCl_2 , in the same container as was used for the SiCl_4 reduction. A closed cycle as described in JP 1997-246853 is not required.

In all of the above-described methods for production of high purity silicon by reduction of SiCl_4 with Zn the ZnCl_2 is leaving the reactor as a gas. The vapour pressure of Zn metal is also significant at the operating temperatures, and some Zn will therefore follow the ZnCl_2 . Furthermore, since the reaction



is not completely shifted to the right at temperatures above the boiling point of ZnCl_2 , the off-gas from the reduction will also contain some SiCl_4 . During cooling of the off-gas, SiCl_4 will react with Zn yielding Si and ZnCl_2 . The prevailing equilibrium
5 conditions in the reactor therefore yield a ZnCl_2 condensate containing both Zn and Si metal. This complicates the recycling of the ZnCl_2 by electrolysis. Furthermore, handling of both liquid and solid Zn and ZnCl_2 is required.

In view of the solutions known from the prior art, the present invention represents a
10 novel and vast improvement of a method and equipment for the production of solar grade (high purity) silicon metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal in liquid state, as the reduction reaction as shown above is completely shifted to the right and as the handling of Zn and ZnCl_2 is minimised. The method according to the invention is effective and the equipment is simple and cheap to build and
15 operate.

The method according to the invention is characterized by the features as defined in the attached independent claim 1.

Further, the equipment according to the invention is characterized by the features as defined in the attached independent claim 11.

20 Claims 2 – 10 and 12 – 19 define advantageous embodiments of the invention.

In the following, the present invention shall be described by examples and figures where:

25 Fig. 1 shows the principal components of a reactor/electrolyser with three compartments according to the present invention shown in a cross sectional end view.

Fig. 2 shows the principal components of the reactor/electrolyser shown in Fig. 1, shown in a cross sectional top view,

30 Fig. 3 shows the principal components of the reactor/electrolyser shown in Fig. 1, shown in one cross sectional side view.

Fig. 4 shows the principal components of the reactor/electrolyser shown in Fig. 1, shown in another cross sectional side view.

Fig. 5 shows a simplified drawing of the material flow in the reactor/electrolyser

It should be understood that the invention is not limited to the design shown in Figures 1-4. The figures are merely presented to exemplify the invention by one possible configuration. With reference to Fig. 1 there is in a cross sectional view shown a reactor/electrolyser with an electrolysis chamber 2, one adjacent chamber 1, and a third chamber 13 for reduction of SiCl_4 by the Zn produced by the electrolysis. Figure 2 shows a top view of the same reactor/electrolyser in the level of the cathodes with the same numerical references. Figure 3 shows a cross section along walls 7 and 8, while Figure 4 shows a cross section along wall 15. In the Figures, reference numerals 3 and 4 are the anodes and cathodes, respectively. In the embodiment shown in the figures, the anodes 3 are inserted through the top being connected to respective electric supply connectors at the top (not further shown), while the cathodes 4 are inserted from the side and being similarly connected to electric supply connectors from the side (neither not shown). It should be understood that the opposite configuration is equally possible, as are configurations with only top inserted electrodes, only side-inserted electrodes, or configurations with bottom-inserted electrodes. For bottom or side inserted electrodes, proper cooling of the electrode head is important to avoid electrolyte leakage from the cell. Bipolar electrode configurations are also possible. In that case, only the mono polar cathode(s) and anode(s) need to be inserted into the cell. Bipolar electrodes also allow for inclination of the electrodes and inclination to nearly horizontal electrode configuration is possible. When using inclined electrodes, chlorine is produced on the electrode surface facing downwards, and Zn on the surface facing upwards.

As Zn is produced, it will, due to its higher density, initially as indicated by numeral 5 be collected on the bottom of the cell in chambers 1 and 2 and then flow through holes 14 in a partition wall 15 down to the bottom of chamber 13. At the upper part of chamber 2 an outlet 6 is provided to collect and evacuate the chlorine being produced under the electrolysis of ZnCl_2 . Openings 9 at the top of the reactor/cell can

be used for the addition of electrolyte components, removal of electrolyte, and inspection of the cell. An opening 10 provided on top of the reduction chamber 13 is mainly used for removal of produced Si 11, but can also be used for addition of Zn if required, as well as addition or removal of other materials and inspection. Reference numerals 7 and 8 are indicating partition walls (in cross sectional view) separating the electrolysis chamber 2 from the middle chamber 1, while reference numeral 15 shows the wall separating the middle chamber from the SiCl_4 reduction chamber. The purpose of the middle chamber 1 is to ensure proper circulation of electrolyte in the electrolysis chamber 2. The chlorine bubbles released on the anode will create an upward flow of electrolyte between the anodes and the cathodes. An opening 19 between the partition walls 7 and 8 allows for a downward flow of electrolyte in chamber 2, thereby creating a circular flow of electrolyte around wall 7 as indicated by the arrow. Such a flow is advantageous for the performance of the ZnCl_2 electrolysis. In chamber 13, reduction of SiCl_4 takes place by bubbling SiCl_4 through the liquid Zn pool 5. SiCl_4 may be fed as a gas or a liquid that will evaporate during feeding. Liquid Zn metal is, as stated above, entering chamber 13 through the holes 14 in wall the 16 and is thereby continuously supplied from the electrolysis chamber 1 to the reduction chamber 13. SiCl_4 is added through tube 12. The tube 12 may have any shape ensuring maximum reaction between SiCl_4 and Zn. One or several tubes, spinning gas dispersers, or manifold designs represent possible examples of solutions to ensure effective distribution of SiCl_4 to the liquid Zn 20 at the bottom of chamber 13. The Si resulting from the reaction between Zn and SiCl_4 is during the process collected as a layer 21 between the electrolyte and the Zn. Typically, the Si layer consists of a mixture of Si and Zn, which can be removed either by pumping or mechanically by grabbing at regular intervals or continuously. The other products from the reaction between SiCl_4 and Zn, ZnCl_2 , dissolves in the electrolyte and is transported by circulation to chamber 1 through the holes 16. From chamber 1 the ZnCl_2 will flow with the electrolyte to chamber 2 where electrolysis of the ZnCl_2 to Zn and Cl_2 takes place.

Figure 3 shows a side view section through partition walls 7 and 8 with the same numerical references as Figs. 1 and 2. By sufficient immersion of the partition wall 8, separation of the atmosphere in chamber 2 is achieved. The electrolysis chamber then contains mainly chlorine, while the adjacent chambers contains mainly air or a

suitable inert gas. The partition wall 7 will assist the generation of circulation of the electrolyte flow indicated by the arrow in Fig. 1. The velocity of the electrolyte can be controlled by adjustment of the gap between the walls 7 and 8, and/or the gap between the wall 7 and the bottom of the cell. With reference to Fig. 3, reference numerals 17 and 18 indicate support pillars for the upper and lower partition walls.

Figure 4 shows a cross section through the wall 15 between chamber 1 and 13. Holes 16 enable flow of electrolyte between chambers 1 and 13, and holes 14 enable Zn to flow between the same chambers.

Figure 5 shows schematically a process sheet of the method according to the invention. As stated above the present invention represent a vast improvement of the previously known methods in that the reduction reaction is completely shifted to the right of the reaction: $\text{SiCl}_4 + 2\text{Zn} = \text{Si} + 2\text{ZnCl}_2$, whereby the handling of Zn and ZnCl_2 is minimised. This is accomplished by conducting electrolysis of ZnCl_2 and reduction of SiCl_4 in a combined, simultaneous process in the same equipment, as is illustrated in the Fig. 5. SiCl_4 reacts with liquid Zn metal whereby Si and ZnCl_2 is produced. ZnCl_2 is in turn circulated to the electrolysis part of the equipment and is conformed to Zn metal which sinks to the bottom of the cell and Cl_2 which suitably is collected and possibly purified and re-used for instance in a process for producing SiCl_4 (not shown in Fig. 5). In such a reactor/electrolyser, ZnCl_2 is electrolysed to Zn and Cl_2 . The chlorine is leaving the reactor/electrolyser as a gas, while the molten Zn metal sinks to the bottom. By a proper design of the reactor/electrolyser, SiCl_4 can be added directly to the Zn pool inside the reactor/electrolyser where it is reduced to Si metal. The ZnCl_2 produced during the reduction will dissolve in the electrolyte and is available for electrolysis. The Si produced in the reactor/electrolyser is removed either continuously or at regular intervals. The chlorine leaving the reactor/electrolyser can e.g. be used for production of SiCl_4 by direct chlorination of impure silicon metal, direct carbochlorination of silica, or for synthesis of HCl that can also be used for chlorination of impure silicon metal.

In the combined reactor/electrolyser, several material choices can be made. Since the purpose of the invention is to produce high purity silicon, materials that do not generate too high contamination of the Si must be used. The anode may preferably

be a carbon material. Graphite is preferred due to its relatively low electrical resistance and its low reactivity towards chlorine. The cathode is also preferably a carbon material, but other electronically conductive materials are not excluded.

- 5 The reactor/electrolyser itself can be made from a steel shell lined with suitable brickwork, e.g. alumina based, silica based, carbon materials, silicon nitride based, silicon carbide based, aluminium nitride based, or combinations of these. It is preferred that the materials in direct contact with the electrolyte or the metal are silicon based, i.e. silica, silicon nitride, silicon carbide, or combinations of these.
- 10 Carbon may also be used where high electrical conductivity is not a problem (e.g. the chamber 13). The same materials may also be used in a reactor without an electrolyser.

- The electrolyte must contain ZnCl_2 . The ZnCl_2 should preferably be free from
- 15 moisture, oxides and hydroxides, but some contaminations can be accepted. In addition, it is preferable to use one or more other chlorides to increase electrical conductivity, reduce the viscosity, hygroscopicity, and the vapour pressure of ZnCl_2 . Typical chlorides that may be added are LiCl , NaCl and KCl , but also alkali earth chlorides such as CaCl_2 and other alkali chlorides can be used. The ZnCl_2
- 20 concentration can range from a few weight percent up to 80 w%. The temperature of the electrolysis can range from the melting point of Zn (420°C) to its boiling point.

- Operation of the reactor/electrolyser is rather straightforward. Before the first start-up, it is necessary to add electrolyte and Zn metal to the cell to the desired levels. The
- 25 electrolysis is preferably run continuously. The SiCl_4 reduction can be run batch-wise or continuously. It is, however, important to ensure a sufficiently stable ZnCl_2 concentration in the electrolyte and Zn metal level in the reactor/electrolyser, and this limits the time between SiCl_4 additions if run in a batch mode. The silicon metal produced is removed at regular intervals. The levels of the Si and electrolyte in the
- 30 reactor/electrolyser determine the maximum time between Si removals. There will be some Zn and electrolyte removed with the Si. These should preferably be recovered by e.g. distillation of the Si. Both Zn and electrolyte components are much more volatile than Si. The recovered electrolyte and Zn can be returned to the reactor/electrolyser. From time to time, it may be necessary to add or remove Zn and

electrolyte from the reactor/electrolyser to account for losses or build-up of such materials. At all time it should be ensured that added materials have the sufficient purity to avoid contamination of the Si produced.

Claims

1. A method for production of high purity silicon (Si) metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal (Zn) in liquid state,
c h a r a c t e r i s e d in that
5 the Zn reduction of SiCl_4 and the production of Zn by electrolysis of ZnCl_2 take place in a common, combined reactor and electrolysis cell using preferably a molten salt as electrolyte
2. A method according to claim 1
10 c h a r a c t e r i s e d in that
 SiCl_4 is fed to the liquid Zn in the combined reactor and electrolysis cell in a continuous or semi-continuous manner as a gas or as a liquid.
3. A method according to claims 1 and 2
15 c h a r a c t e r i s e d in that
 SiCl_4 is fed to the liquid Zn through one or several lances.
4. A method according to claims 1 and 2
c h a r a c t e r i s e d in that
20 SiCl_4 is fed to the liquid Zn through a spinning gas disperser.
5. A method according to claims 1 and 2
c h a r a c t e r i s e d in that
 SiCl_4 is fed to the liquid Zn through a manifold with several gas exit holes.
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6. A method according to claims 1-5
c h a r a c t e r i s e d in that
the produced Si is removed from the cell by means of pumping..

7. A method according to claims 1-5
characterised in that
5 the produced Si is removed mechanically from the cell by means of a grabbing device.
8. A method according to claims 1-7
characterised in that
10 the operating temperature lies between the melting and boiling point of Zn
9. A method according to claims 1-8
characterised in that
ZnCl₂ is dissolved in the molten salt comprising any of the alkali halides, any of
15 the alkali earth halides, or a mixture thereof.
10. A method according to claims 1-9
characterised in that
the chlorine produced by the electrolysis of ZnCl₂ is purified to be reused for the
20 production of SiCl₄.
11. Equipment for production of high purity silicon (Si) metal from reduction of silicon tetrachloride (SiCl₄) by zinc metal
characterised in that
25 the Zn reduction of SiCl₄ and the production of Zn by electrolysis of ZnCl₂ take place in a common, combined reactor and electrolysis cell using a molten salt as electrolyte.
12. Equipment according to claim 11
30 characterised in that
the reactor and electrolysis cell are provided in a common housing which is divided into two or more communicating compartments (13, 1, 2) by first or more partition walls (15, 8, 7), where the electrolysis of ZnCl₂ by means of electrodes (3, 4) is taking place in at least one compartment (1, 2) and the Zn reduction of

SiCl₄ takes place in at least one other compartment (13), and where Zn metal flows between the chamber/s (1,2) of the ZnCl₂ electrolysis to the chamber/s (13) of SiCl₄ reduction, and where the electrolyte circulates between the chamber/s of ZnCl₂ electrolysis to the chamber/s of SiCl₄ reduction, and where the atmosphere in the chamber/s where electrolysis take place are separated from the atmosphere in the other chambers by the first partition wall (15).

13. Equipment according to claims 11-12

characterised in that

the electrolysis is performed by means of at least two monopolar electrodes.

14. Equipment according to claims 11-12

characterised in that

the electrolysis is carried out using at least two monopolar electrodes and one or more bipolar electrodes.

15. Equipment according to claims 11-14,

characterised in that

the monopolar electrodes are cooled by a cooling medium such as water.

16. Equipment according to claims 11-14,

characterised in that

the electrodes are based upon a graphitic material.

17. Equipment according to claims 11-16,

characterised in that

the material in the reactor's and/or electrolyser's lining is containing more than 50% SiO₂

18. Equipment according to claims 11-16,

characterised in that

the material in the reactor's and/or electrolyser's lining is contains more than 5% silicon nitride

19. Equipment according to claims 11-16,
c h a r a c t e r i s e d in that
the material in the reactor's and/or electrolyser's lining is contains more than 5%
silicon carbide