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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 solar grade (high purity) silicon metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal in liquid state.

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 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.

The presently known 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

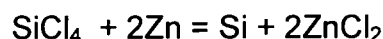
much larger scale. Gaseous SiCl_4 and gaseous Zn was fed to a fluidised bed reactor, where Si granules were formed (see e.g. D.A. Seifert and M. Browning, AIChE Symposium Series (1982), 78(216), p.104-115). Reduction of SiCl_4 in molten Zn has also been described in various patents. US4,225,367 describes a process for

5 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. JP1997-246853,

“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.

15 A similar process is described in WO2006/100114. A difference between this and JP1997-246853 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 JP1997-246853 is not required.

20 In all of the above-described known 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-
30 gas, SiCl_4 will react with Zn yielding Si and ZnCl_2 . The prevailing equilibrium conditions in the reactor therefore yield a ZnCl_2 condensate containing both Zn and Si metal.

In view of the solutions known from the prior art, the present invention represents a novel and vast improvement of a method and equipment for the production of 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. The method according to the invention is effective and the equipment is simple and cheap to build and 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. Claims 2 – 10 and 12 – 19 define advantageous embodiments of the invention.

In the following, the present invention shall be described by way of example and with reference to the attached Fig. 1, which shows a principal sketch of a reactor according to the present invention in cross sectional side view.

With reference to Fig. 1 there is shown a reactor 5 for reduction of SiCl_4 by Zn containing beyond a Zn pool 1 at the bottom of the reactor, a liquid layer of Si above the liquid Zn pool and a layer of a suitable salt 3 on top of the Si. In the reactor, reduction of SiCl_4 takes place by bubbling SiCl_4 via a tube, lance or the like 4 through a liquid Zn pool 1 at the bottom of the reactor 5. SiCl_4 may be fed as a gas or a liquid that will evaporate during feeding. Zn metal is added to the reactor either as a liquid or a solid, which in turn will melt due to the existing temperature in the reactor. The tube 4 may have any shape ensuring good 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 1 at the bottom of the reactor 5. The Si resulting from the reaction between Zn and SiCl_4 is during the process collected as a layer 2 between the molten salt 3 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 product from the reaction between SiCl_4 and Zn, ZnCl_2 , dissolves in the molten salt 3 and thereby enriches the molten salt during operation (the reduction process). The molten salt thus enriched with ZnCl_2 can be removed by pumping, grabbing or by flow through suitable channels or tubes. To replace the removed salt,

molten salt containing less or no ZnCl_2 may be added to the reactor by pumping, pouring or by flow through suitable channels or tubes.

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: $\text{SiCl}_4 + 2\text{Zn} = \text{Si} + 2\text{ZnCl}_2$. This is accomplished by performing the reduction in contact with a molten salt able to dissolve the formed ZnCl_2 . The molten salt has a lower density than the molten Zn where the reduction reaction is taking place and will therefore float on top of the liquid Zn. The ZnCl_2 released during the reduction will float or boil to the top of the metal where it will dissolve in the molten salt. If the temperature of the ZnCl_2 is below the normal melting point it will float, whereas if it is above the boiling point it will rise as bubbles (boil). In either case, the ZnCl_2 will dissolve in the molten salt. The ZnCl_2 therefore remains in the liquid state rather than evaporate as is known from the prior art. ZnCl_2 remains liquid even at temperatures above its normal boiling point. The molten salt also serves to create a barrier between the produced Si and the surrounding atmosphere, thereby preventing oxidation. The molten salt is preferably chloride based, typically consisting of alkali chlorides, alkali earth chlorides, or a mixture thereof. The reduction may be performed both above and below the normal boiling temperature of ZnCl_2 . However, the temperature should preferably lie between the normal melting and boiling point of Zn. The molten salt may be the same as that used for molten salt electrolysis of ZnCl_2 . The Si produced in the reactor may be removed either continuously or at regular intervals. The molten salt containing the produced ZnCl_2 can be removed either continuously or at regular intervals. It is necessary to replace the molten salt that is removed from the reactor. This can be done either continuously or at regular intervals

As to the design and construction of the reactor 5, 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 reactor can be 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 molten salt or the

metal are silicon based, i.e. silica, silicon nitride, silicon carbide, or combinations of these. Carbon may also be used.

Even though not shown in Fig. 1, it must also be possible to supply heat (energy) to the reactor. Thus, heating can be accomplished by placing the reactor in a suitable furnace. Induction heating of the molten Zn is also possible, as is resistance heating by passing an electric current through the molten salt.

The reaction $\text{SiCl}_4(\text{g}) + \text{Zn}(\text{l}) = 2\text{ZnCl}_2(\text{l}) + \text{Si}(\text{s})$ is slightly exothermic (-130 kJ/mol at 800°C). During the reduction, the temperature of the molten salt will therefore increase. If the reactor is operated in batch mode, the temperature increase can be controlled by the amount of molten salt relative to the amount of SiCl_4 reacted. The temperature may be brought down again by replacing the ZnCl_2 enriched molten salt by a colder molten salt, or by adding frozen salt. Internal cooling by e.g. coils (not shown in Fig. 1) carrying a suitable cooling medium is also possible. If the reactor is operated in a continuous mode, the temperature can be maintained by adding sufficiently cold molten salt, or by adding a sufficient fraction of frozen salt.

The molten salt typically contains chlorides such as LiCl, NaCl and KCl, but also alkali earth chlorides such as CaCl_2 and other alkali chlorides can be used. Fluoride salts can also be added. The temperature of the reduction can range from the melting point of Zn (420°C) to the normal boiling point of Zn (907°C).

The Zn metal can be regenerated by electrolysis (neither not shown) the ZnCl_2 in the molten salt, preferably by direct electrolysis of the molten salt. The molten salt from the reactor is then used as feed for the electrolysis cell(s). Electrolyte from the electrolysis cell(s) may be used to replace the molten salt in the reactor. In this case, a molten salt enriched with ZnCl_2 is fed to the electrolysis cell where ZnCl_2 is electrolysed to Zn metal and chlorine gas, thereby lowering the concentration of ZnCl_2 in the molten salt, which is returned to the reactor. The Zn may also be added to the reactor, while the chlorine can be used for other purposes, e.g. for production of SiCl_4 . The equipment may be designed such that the molten salt may flow between the reactor and the electrolysis cell in suitable tubes or channels (not shown). If required, the molten salt can be cooled or heated during transport from the

reactor to the electrolysis cell, and vice versa (neither not shown). When Zn is to be regenerated by molten salt electrolysis of ZnCl_2 , the present invention has further advantages compared to the prior art. Pure ZnCl_2 is very hygroscopic, has a high vapour pressure and high viscosity in the molten state. On the other hand, the salt
5 containing ZnCl_2 is not very hygroscopic, has a low vapour pressure and viscosity in the molten state. Handling of the salt containing ZnCl_2 is therefore easier than handling pure ZnCl_2 .

Operation of the reactor is rather straightforward. Before the first start-up, it is necessary to add molten and Zn metal to the reactor to the desired levels. Then SiCl_4
10 is added. The SiCl_4 reduction can be run batch-wise or continuously. It is important to ensure that the ZnCl_2 concentration in the molten salt does not get too high, as this may lead to excessive ZnCl_2 evaporation. In a batch mode operation, this limits the amount of SiCl_4 added before molten salt must be removed. The silicon metal produced is removed at regular intervals. The levels of the Si and molten salt in the reactor
15 determine the maximum time between Si removals. There will be some Zn and molten salt removed with the Si. These constituents should preferably be recovered by e.g. distillation of the Si. Both Zn and molten salt components are much more volatile than Si. The recovered molten salt and Zn can be returned to the reactor. From time to time, it may be necessary to add or remove Zn and molten salt from the
20 reactor to account for losses or build-up of such materials. At all times it should be ensured that added materials have the sufficient purity to avoid contamination of the Si produced.

Claims

1. A method for batch wise or continuous production of high purity silicon (Si) metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal (Zn) in liquid state in a reactor (5),
5 c h a r a c t e r i s e d i n t h a t
the Zn reduction of SiCl_4 takes place in the reactor (5) containing, in addition to Si and Zn a molten salt and ZnCl_2 dissolved in the salt.
2. A method according to claim 1
10 c h a r a c t e r i s e d i n t h a t
 SiCl_4 is fed 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 i n t h a t
 SiCl_4 is fed to the liquid Zn through one or several lances.
4. A method according to claims 1 and 2
20 c h a r a c t e r i s e d i n t h a t
 SiCl_4 is fed to the liquid Zn through a spinning gas disperser.
5. A method according to claims 1 and 2
25 c h a r a c t e r i s e d i n t h a t
 SiCl_4 is fed to the liquid Zn through a manifold with several gas exit holes.
6. A method according to claims 1-5
30 c h a r a c t e r i s e d i n t h a t
the produced Si is removed by means of pumping.
7. A method according to claims 1-5
30 c h a r a c t e r i s e d i n t h a t
the produced Si is removed mechanically by means of grabbing.

8. A method according to claims 1-7

characterised in that

the operating temperature is held between the melting and normal boiling point of Zn

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9. A method according to claims 1-8

characterised in that

the molten salt comprises any of the alkali halides, any of the alkali earth halides, or a mixture thereof

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10. A method according to claims 1-9

characterised in that

the molten salt containing the ZnCl_2 produced by the reduction reaction is used as feed to a molten salt electrolysis cell to regenerate the Zn metal.

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11. Equipment for batch wise or continuous production of high purity silicon (Si)

metal from reduction of silicon tetrachloride (SiCl_4) by zinc metal in a reactor

characterised in that

the Zn reduction of SiCl_4 takes place in the reactor containing in addition to Si and Zn a molten salt and ZnCl_2 dissolved in the salt

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12. Equipment according to claim 11,

characterised in that

the material in the reactor's and/or electrolyser's lining contains more than 50% SiO_2 .

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13. Equipment according to claim 11,

characterised in that

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

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14. Equipment according to claims 11,

characterised in that

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

silicon carbide.

15. Equipment according to claim 11,

C h a r a c t e r i s e d in that

5 the reactor's and/or electrolyser's lining contains more than 5% graphitic material.

16. Equipment according to claim 11,

c h a r a c t e r i s e d in that

10 the feeding device for the SiCl_4 is made of a graphitic material.

17. Equipment according to claim 11,

c h a r a c t e r i s e d in that

15 the feeding device for the SiCl_4 is made of a silica based material

18. Equipment according to claim 11,

c h a r a c t e r i s e d in that

the feeding device for the SiCl_4 is made of a silicon nitride based material

19. Equipment according to claim 11,

c h a r a c t e r i s e d in that

20 the feeding device for the SiCl_4 is made of a silicon carbide based material