Low-Temperature Fused Salt Electrolysis of Quartz

The present invention pertains to a process for preparing silicon.

Three forms of silicon are offered on the global market: in addition to silicon as an alloy component and technical silicon ("metallurgical grade"), pure silicon ("electronic grade") as the third offered form is of great and increasing importance. The latter is used in semiconductor technology; this product sector makes high demands on the degree of purity and the quality.

In the last 25 years the production of pure silicon has strongly increased. In 1980, the annual production was 3000 t, in 1997 it was 20,000 t. The degree of purity, the crystal structure (amorphous, polycrystalline, monocrystalline) and the production costs are the three decisive criteria in the technical-industrial application.

The price for pure silicon depends on the degree of purity and the crystalline structure thereof. In 1997, 1 kg of polycrystalline silicon cost approximately € 40.00, monocrystalline silicon approximately € 300.00 and high-purity silicon used in semiconductor technology as so-called "Si wafers" approximately € 8,500.00.

Silicon has to be of the highest purity to show semiconduction properties. The resistivity of elemental silicon is stated to be $1 \cdot 10^{10}$ Ω•cm, sometimes also $1 \cdot 10^{18}$ Ω•cm. Technically manufactured pure silicon has a value of up to 150,000 Ω•cm.

Pure silicon requires especially low boron and phosphorous contents. Typically, degrees of purity of from 0.1 to 1 ppb are required. Resistivity

should not be below 100 Ω•cm. The higher the resistivity, the higher the purity is.

Pure silicon is prepared from technical silicon. The preparation of technical silicon proceeds by reducing quartzites with coke in electric-arc furnaces (carbothermal reduction) resulting in a silicon yield of 80 %, based on SiO_2 of the starting material. The high operating temperature of approximately 2000 °C also results in a high energy demand of from approximately 11 to 14 MWh/t of silicon.

The silicon so obtained is ground and purified in an acid bath and by washing. Thereafter, two different manufacturing processes may be employed to purify said silicon to pure silicon. About three quarters of the world production are obtained by the so-called "Siemens C process". The preparation in pure state is performed using either trichlorosilane ($HSiCl_3$) or silane (SiH_4). High degrees of purity may be achieved by crude and precision distillations of said trichlorosilane or silane.

Trichlorosilane is obtained by reacting technical silicon with hydrogen chloride in a fluidized bed reactor.

Polycrystalline pure silicon is obtained by a pyrolytic decomposition of trichlorosilane at a temperature of 1000 °C on thin rods made from pure silicon. Observing tedious safety requirements, the yield may be increased in a hydrogen atmosphere. However, also the distillate so obtained frequently contains a certain amount of boron trichloride. Hence, the resistivity of the silicon made therefrom will not exceed 1500 Ω•cm.

Another purification method proceeds via silicon tetrafluoride. In this method silicon tetrafluoride is reacted with sodium aluminium hydride to form silane which is subsequently subjected to pyrolysis at a temperature of approximately 800 °C. Due to the chemical instability of silane and the hazard of explosion associated therewith, tedious safety requirements are also to be

observed. This production method yields high-purity silicon beads having diameters of from 1 to 3 mm as a product.

Due to the high energy requirement a need for processes for preparing silicon, in particular pure silicon which have lower energy requirements and cause as little environmental pollution as possible persists.

In particular, it is the object of the present invention to provide processes overcoming the drawbacks of prior art.

The problem is solved by a process for preparing silicon comprising the following steps:

a) fused salt electrolysis of an SiO_2-containing starting material together with antimony, mercury and sulfur to obtain a decomposed material;

b) washing to remove elemental sulfur;

c) acid treatment to eliminate foreign ions;

d) reduction treatment to reduce mercury and/or antimony salts;

e) density separation to separate the silicon from the residual components.

The essential component of the process is a fused salt electrolysis proceeding at relatively low temperatures.

According to the invention, SiO_2 (quartz, sand) is subjected to a fused salt electrolysis together with antimony, mercury and sulfur. Presumably, essentially the following steps proceed during the fused salt electrolysis:

1) sulfur (in the form of S_6 and S_8 molecules) is oxidized at the positive terminal to form divalent polysulfide cations:

$$S_x \rightarrow S_x^{2+} + 2\ e^-$$

2) These sulfur cations oxidize elemental mercury:

$$S_x^{2+} + Hg \rightarrow Sx + Hg^{2+}$$

3) The Hg cations react with elemental antimony:

$$3\ Hg^{2+} + 2\ Sb \rightarrow 3\ Hg + 2\ Sb^{3+}$$

This step results in an in-process recovery of elemental mercury already during fused salt electrolysis.

4) In the liquid melt antimony cations and sulfur anions form antimony(III) sulfide, a black, sparingly soluble solid, according to:

$$2\ Sb^{3+} + 3\ S^{2-} \rightarrow Sb_2S_3$$

High field strengths may result in the formation of antimony(V) sulfide and mercury(II) sulfide, which is unwanted.

In the negative terminal region presumably the following steps proceed:

5) sulfur is reduced

$$S_x + 2\ e^- \rightarrow S_x^{2-}$$

These polysulfide anions attack the silicon atoms within the SiO_2 lattice. In this reaction the Si-O bond is heterolytically cleaved.

6) The Si cations react with the polysulfide anions in a redox reaction. Elemental silicon and elemental sulfur are formed:

$$Si^{4+} + 2\ [S_x^{2-}] \rightarrow Si + 2\ S_x$$

Presumably, this is catalytically promoted by antimony(III) sulfide.

7) Sb_2S_3 also reacts with oxide anions according to the following reaction:

$$6\ O^{2-} + 2\ Sb_2S_3 \rightarrow 3\ O_2 + 4\ Sb + 6\ S^{2-}$$

In this fused salt electrolysis process the molar fractions of silicon, sulfur, antimony and mercury are preferably selected as follows:

- SiO_2 : S = from 1:4 to 1:6

- SiO_2 : Sb = from 1:0.4 to 1:0.6 and/or

- SiO_2 : Hg = from 1:1 to 1:1.3.

For fused salt electrolysis, a field strength in the range of from 0.1 to 0.5 V/m is especially well suited with values from 0.1 to 0.3 V/m being more preferred. The mixture of substances is heated as uniformly as possible and melts in a temperature range of from 110 to 120 °C. Preferably, the temperature is subsequently raised to 125 °C. These conditions should be maintained for several minutes. The electrochemical reactions are completed when the voltage increases. An additional residence time of at least 30 min has been found advantageous to increase the yield.

Next, a washing step is performed to remove the elemental sulfur. Any solvents having a good solubility for sulfur (S_x) are especially suited. A good solubility means that a solubility of at least 10 g of S_x in 100 g of solvent (a total of 110 g) is achieved at 20 °C. Said solvents are exemplified by carbon disulfide (CS_2), guanidine (CH_5N_3), thiazole (C_3H_3NS), thiophene (C_4H_4S), dioxan ($C_4H_8O_4$) and mixtures thereof.

Prior to washing, the material may be mechanically crushed. Suitable particle sizes range from 0.2 to 15 mm. In one embodiment the preferred range is from 2 to 15 mm, in another from 0.4 to 4 mm. Observations have shown

that washing is improved by using small particle sizes. Preferably, several washing steps are performed and the obtained material is agitated together with the solvent for some time before separating it off. Depending on the solvent type, from 0.8 to 9 kg (approximately from 1 to 12 l) of solvent, e.g., carbon disulfide, are required for 1 mol of SiO_2. The used solvents should be of high purity.

Subsequently, the solvent and the sulfur removed by the solvent may reused.

After washing and separating off the material, the residual solvent is preferably volatilized. This may be favored by applying a vacuum.

An acid treatment is performed as the next step. Strong acids having pH values of from approximately -1.0 to -1.6 are suitable. For example, mixtures of nitric acid with additional acids, e.g., sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, chloric acid, chlorous acid, hydrobromic acid, bromic acid, methane acid or mixtures of said acids are suitable.

The chemical degree of purity of the acids should be high. Suitable amounts for 1 mol of SiO_2 range from 2 to 7, preferably from 3 to 4 l of acids. Preferably, the mixture should be stirred for some time, e.g., from 10 to 20 min.

Without being bound to this theory, it is supposed that the acid enables unwanted cations, e.g., boron, magnesium, calcium, aluminium and iron and anions such as phosphate, bromide, iodide to be dissolved out. Optionally, a preceding oxidation of any existing impurities is required for this.

Sediment and supernatant are separated. Optionally, sulfur and acids may be recovered from the supernatant and thus reused (regenerated). If the acid separation is not complete, it may be appropriate to perform one or several washing steps with distilled water. Typical amounts range from 2 to 5 l per mol of SiO_2.

The next step to follow is a reducing step to convert the unwanted solids HgS and Sb_2S_5 into Hg and Sb, resp. Suitable reducing agents are those having redox potentials in the order of approximately 1.6 V to 1.8 V, preferably approximately 1.74 V in particular in aqueous salt solutions. A sodium dithionite solution is a suitable substance.

Subsequent to optional washing steps the sediment of the last process step is treated in the reducing agent for some time, e.g., stirred for 10 min. Suitable concentrations of the molarity of the reducing agent, e.g., sodium dithionite, are within the range from 0.3 to 1.2 mol/l, preferably 0.5 mol/l. A suitable liquid volume is from approximately 1 to 5 l, preferably approximately 2.5 l per mol of SiO_2. It this step the solution may be slightly heated; the temperature is preferably from room temperature to 60 °C, more preferably from 50 to 60 °C.

Subsequent to the treatment with said reducing agents washing steps may follow again. Suitable water amounts range from 2 to 5 l per mol of SiO_2. Amongst others, the remaining sediment contains Hg, Sb, Sb_2S_3 and residual amounts of SiO_2 in addition to silicon.

This is followed by a drying step and, depending on the sediment state, optionally a size reduction. Typically suited particle sizes range from 0.2 to 3 mm with ranges from 0.5 and 3 mm and from 0.8 and 2 mm being preferred. However, particle sizes from 0.4 to 0.8 mm are especially preferred.

A density separation follows as the next step. Silicon has the lowest specific weight of the contained solids (density of pure silicon: 2.33 $g \bullet cm^{-3}$).

In a preferred embodiment the density separation is performed as a density centrifugation especially in trichlorosilane. At 15 °C said liquid has a density of 2.36 $g \bullet cm^{-3}$ resulting in the residual metallic, oxidic and sulfidic components settling on the bottom. This may be accelerated by centrifugation. The resulting floating silicon (poly- and monocrystalline silicon) may be separated

off and liberated from trichlorosilane, e.g., under vacuum. Subsequent to the trichlorosilane removal, also the precipitate may be added to the next fused salt electrolysis operation in the form of a solid mixture.

The process of the invention has numerous advantages, in particular the suitability of using purified sand/quartz as starting material. Said sand/quartz should only be sieved to a certain particle size and washed. It is not necessary to use technical silicon.

Moreover, the purification uses substances which are well available on the one hand and recovered in the process on the other hand such that practically no waste materials are formed apart from extremely small amounts.

Compared to prior art processes, the present manufacturing process is energy-saving due to the distinctly lower process temperatures. It is estimated that compared to prior art the expenditure of energy is less that 20%, rather in the order of 10%. Also in this case silicon is obtained in a good yield of approximately 80% and more.

The process of the invention yields pure silicon having a high degree of purity. The electrical resistivity may exceed 6000 Ω•cm, optionally also 8000 Ω•cm.

The amount of monocrystalline silicon is high, e.g., greater than 50%, preferably greater than 80%. Since a hydrogen atmosphere or the like is not required, the facility does not require particular safety measures. The facilities are much less technically complex than prior art facilities.

The present invention will be further illustrated by the following example.

Example 1

Purified sand twice washed with water was sieved to a particle size of from 0.3 to 0.8 mm in diameter. In combination with powdery sulfur and powdery

antimony having particle sizes of 0.3 mm maximum, a solid mixture as uniform as possible was prepared. The molar proportions were

SiO_2:S:Sb:Hg = 1:5.2:0.52:1.15.

The mixture was transferred into a vessel made from iron (C content <1.5%) and heated. The mixture began to melt eutectically at 110 °C.

The viscous melt appeared to be dull gray. Fused salt electrolysis was initiated at a temperature of approximately 115 °C. The iron vessel was the negative terminal, whereas an electroconductive injection device (a tube of 0.2 mm in diameter) dipping into the melt was the positive terminal with mercury flowing through said tube into the molten liquid with uniform speed during electrolysis. In this process a temperature increase to approximately 119 °C was observed.

A voltage of 5.1 V was applied as starting voltage. The electrochemical reaction started when mercury flowed into the melt and the voltage dropped to a range of between 1.1 and 0.6 V. The current varied within a range of from 0.3 to 1.5 A. A production of gas identified as oxygen was observed. The process was controlled by the field strength, which was preset to 0.22 $V \bullet m^{-1}$.

Subsequent to the introduction of mercury the temperature within the iron vessel was increased to approximately 125 °C. During this increase the electrical field conditions were kept constant for 5 min. The voltage increased to approximately 1.8 V. Then it increased abruptly to a value slightly exceeding 5 V. Thereupon electrolysis was stopped. The temperature conditions were kept for approximately 30 min. Then, the melt had a crystalline, silvery gray surface. Below a grayish black (anthracite colored) regulus had settled. The majority of the elemental mercury had accumulated in puddles and lenses and could directly be collected by suction. The complete

regulus containing residual mercury droplets and lenses was transferred into an inert reaction vessel.

Example 2 - Washing Step

The material obtained in example 1 was crushed to a particle size of from approximately 2 to 13 mm. Then, it was stirred with 1.5 l of carbon disulfide for 10 min. The supernatant was separated off and again washed with 1.5 l of carbon disulfide. The supernatant was again separated off, combined with the first supernatant and fed to sulfur recycling.

The residual solvent was evaporated from the sediment by slightly heating the sediment (temperature <50 °C).

Example 3

The dried sediment so obtained was subjected to an acid bath in an inert vessel. A mixture of aqueous nitric acid having a final concentration of 41% by weight and aqueous sulfuric acid having a final concentration of 23% by weight was used as the acid. The sediment was washed with 3.7 l of said acid mixture by stirring it for 10 to 20 min. In this process an evolution of nitrous gases was observed which may be associated, e.g., with an oxidation of bromide to bromate. The slightly milky acid supernatant was separated off. The liquid phase contained colloidally suspended sulfur which was recycled just as the acid.

Subsequently, the black sediment partially covered with a gray white coating was twice washed with distilled water at room temperature by stirring the sediment with 2.8 l of water for approximately 10 min and separating off the supernatant.

Example 4

The precipitate obtained from the acid bath was stirred with 2.5 l of a 0.5 mol/l solution of sodium dithionite for 10 min. The solution was adjusted (heated) to a temperature of approximately 53 °C. Two washing steps with 2.8 l of water and a separation of the supernatant followed.

The precipitate was dried at approximately 40 °C and mechanically crushed to a particle size in the range <2 mm.

Example 5

The solid mixture of example 4 was mixed with trichlorosilane and subjected to a centrifugation at 500 • g at 15 °C for 5 min. The material floating at the top was skimmed off and dried at a temperature of 40 °C and a reduced pressure of 30 hPa. The centrifugation precipitate was fed to the overall process as starting material.

Claims

1. A process for preparing silicon comprising the following steps

   a) fused salt electrolysis of an SiO_2-containing starting material together with antimony, mercury and sulfur to obtain a decomposed material;

   b) washing to remove elemental sulfur;

   c) acid treatment to eliminate foreign ions;

   d) reduction treatment to reduce mercury and/or antimony salts;

   e) density separation to separate the silicon from the residual components.

2. The process according to claim 1, wherein the molar fractions of step a) are selected as follows:

   SiO_2: S = from 1:4 to 1:6

   SiO_2 : Sb = from 1:0.4 to 1:0.6 and/or

   SiO_2 : Hg = from 1:1 to 1:1.3.

3. The process according to claim 1 or 2, wherein the fused salt electrolysis of step a) is performed at a field strength in the range of from 0.1 to 0.5 V/m.

4. The process according to any one of claims 1 to 3, wherein the washing step b) is performed by washing with carbon disulfide, guanidine, thiazole, thiophene, dioxan or mixtures thereof.

5. The process according to any one of claims 1 to 4, wherein the acid treatment is performed with a mixture of nitric acid and an acid selected from sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, chloric acid, chlorous acid, hydrobromic acid, bromic acid, methane acid.

6. The process according to any one of claims 1 to 5, wherein the reduction is performed with an aqueous sodium dithionite solution.

7. The process according to any one of claims 1 to 6, wherein the density separation is performed by a density centrifugation in trichlorosilane.

8. The process according to any one of claims 1 to 7, wherein the fused salt electrolysis is performed in a vessel made from iron.

9. The process according to any one of claims 1 to 8, wherein the soluble material is crushed after step a) and/or after step d).

10. The process according to any one of claims 1 to 9, wherein a water washing is performed after step c) and/or step d).

11. The process according to any one of claims 1 to 10, wherein separated amounts of acids, solvents, sulfur, mercury, mercury compounds, antimony and/or antimony compounds are processed and reused.