



**NORWEGIAN UNIVERSITY OF SCIENCE AND  
TECHNOLOGY**

Faculty of Natural Science and Technology  
Department of Materials Science and Engineering

# **Refining and Recycling of Silicon: A Review**

ARJAN CIFTJA

THORVALD ABEL ENGH

MERETE TANGSTAD

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# INTRODUCTION

Silicon has a very broad spectrum of usage nowadays and it lies at the heart of much modern technology. It is the most abundant element in the earth's crust after oxygen. Indeed, its use ranges from such bulk commodities as concrete, clays and ceramics, through more chemically modified systems such as soluble silicates, glasses and glazes to the recent industries based on silicone polymers and solid-state electronics devices. The refined technology of ultrapure silicon itself is perhaps the most elegant example of the close relation between chemistry and solid-state physics and has led to numerous developments such as the transistor, printed circuits and microelectronics.

Three major applications have since greatly stimulated the production and purification of silicon, that is, as an alloy in aluminium, silicones and solid-state electronics. Silicon carbide has also found a broad range of applications taking advantage of its hardness and chemical noble character.

Over the past years, the photovoltaic industry has been experiencing a strong economic growth world-wide. This expansion is due to an increasing demand for PV modules which is expected to continue in the coming years. Since the dominant semiconductor material used in photovoltaics is silicon, in this literature review emphasis is put on the recycling and refining of silicon for photovoltaics (PV).

## 1 SILICON

Silicon (Si) is the second member in the Group IVA in the periodic system of elements. It never occurs free in nature, but in combination with oxygen forming oxides and silicates. Most of the Earth's crust is made up of silica and miscellaneous silicates associated with aluminium, magnesium and other elements. Silicon constitutes about 27% of the Earth's crust and is the second most abundant element in mass, after oxygen [1].

## 2 HISTORY AND APPLICATION OF SILICON

Since antiquity, silicon has been of great importance to humanity. However, the first applications were based on naturally occurring forms of silicon, for instance, flint (silex/silicis in Latin), a variety of quartz used from the Stone Age to the Neolithic Era to make tools, weapons and later potteries. Glass made of silicate dated back to 12 000 B.C. The great affinity of silicon for oxygen delayed its isolation as the free element until 1823 when Berzelius [1] prepared it for the first time, passing silicon tetrachloride over heated potassium. Silicon tetrachloride could be prepared by chlorinating silicate/silica. The first crystalline silicon was made accidentally in 1854 by Sainte-Claire Deville working on aluminium electrolysis. The first preparation of silicon/ silicon rich alloys in an electric arc furnace was performed by Moisan in 1895 and the industrial production was by Bozel and Rathenau independently from 1897 to 1898. Acheson also discovered accidentally in this period silicon carbide while trying to make artificial diamond. Silicon alloys, particularly ferroalloys, have from the end of the nineteenth (XIX) century played an important role in the production of steel. Silicon metal (silicon content higher than 96% according to definitions outlined by the trade organizations) was not current until the Second World War [2]. Three major applications have since greatly stimulated the production and purification of silicon, that is, alloy in aluminium, silicones and solid-state electronics. Silicon carbide has also found a broad range of applications taking advantage of its hardness and chemical noble character. More recently SiC has found applications in electronics because of its excellent semiconductor properties and tends to become a strategic material for cutting silicon and boules into thin wafers.

At the beginning of the new 2000 millennium, approximately one million metric tons of metallurgical grade silicon, also called *silicon metal* in the industry because of its appearance and not because of its physical properties, are produced and sold in the world market. This is a relatively small amount compared to the multimillion metric ton markets of crude iron, steel, aluminium or ferroalloys. Industrial location to produce silicon metal has been guided by the vicinity of rich and pure quartz deposits and/or the availability of abundant electrical power. Leading producing countries are PR China, the United States, Brazil, Norway and France. In spite of some recent mergers, the industry remains fragmented.

The silicon metal market is traditionally divided into two main subgroups, that is, the aluminium and the chemical segments each consuming approximately half of the worldwide output. There are, however, some differences in the characteristics requested by each [2].

## **2.1 ALLOY IN ALUMINIUM**

In the aluminium industry, silicon is added to molten aluminium in which it is dissolved. A simple eutectic composition occurs at 12.6% silicon in aluminium. This has important consequences for industrial applications in the aluminium industry. Silicon is used in order to improve the viscosity, the fluidity of liquid aluminium and the mechanical properties of commercial alloys. The iron, calcium and phosphorus content in silicon are particularly critical for such applications.

There are two important groups of aluminium alloys in which silicon is one of the main alloying elements.

### *Casting alloys*

By adding silicon to the melt, the fluidity is improved. Aluminium alloys near the eutectic composition are therefore used in thin-walled castings. Typical concentrations are 7 to 12%. If a few tenths of a percent of magnesium is added, the alloys may be age-hardened and thereby nearly double their yield strength.

To counteract the formation of large needle-shaped particles, the alloys are normally modified with sodium, strontium or phosphorus. The alloys present good corrosion properties.

### *Wrought alloys*

AlMgSi alloys (6xxx series) are widely used as medium-strength structural alloys. Typical silicon content is 0.5 to 1.0%.

The alloys of the 6xxx series have good hot-working properties and are agehardening. These alloys are therefore well suited for extrusion of profiles, which by heating at 150 to 200°C are given their final strength.

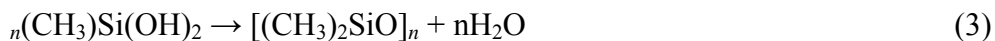
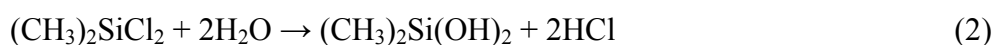
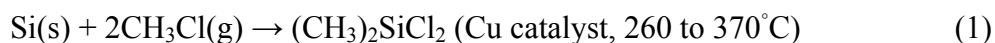
The alloys present good corrosion and weldable properties. Typical markets are building and transport industries [2].

## **2.2 APPLICATIONS IN CHEMISTRY**

### *Silicones*

Since the discovery of the direct synthesis (reaction 1) of dimethyldichlorosilane, during the Second World War independently by Rochow and Müller, the silicone industry has

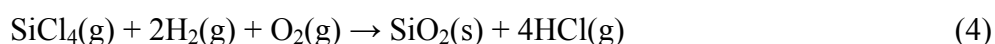
developed to become a strong and growing chemical business consuming (year 2000) about 400 000 MT of silicon [2 - 4].



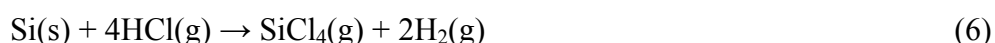
The direct synthesis (1) is industrially performed in a fluidized bed reactor requiring small particles or powder of silicon (20–300  $\mu\text{m}$ ). The reaction is exothermic and needs to be activated with copper catalysts as well as promoters Zn, Sn, P and others. Whereas Fe does not seem to play an important role, Ca and Al have shown to take an active part in the overall reaction.

#### *Synthetic silica*

Various synthetic silica such as pyrogenic silica (also called *fumed silica*) or silica ingots as feedstock to optical fibers are industrially prepared by burning silicon tetrachloride [3]:



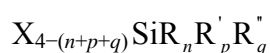
Silicon tetrachloride may be prepared by chlorination of natural silica. However, industrially, silicon tetrachloride is produced by reacting chlorine with metallurgical grade silicon in a direct synthesis performed either in a fluidised bed or a fixed bed reactor:



The present fumed silica market is about 100 000 to 120 000 MT, which in turn consumes around 50 000 to 60 000 MT of metallurgical silicon. It is noted that the main market for fumed silica is as additives in silicone rubbers used to increase the mechanical strength and the elasticity of these elastomers.

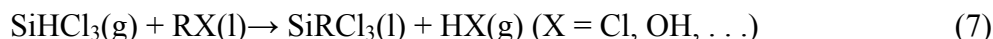
#### *Functional silanes*

This generic term covers a broad range of products built on silane molecules, in which an atom of hydrogen or of chlorine is substituted with an organic radical bearing a functional group, for example, amine, acid, ester, alcohol and so on.

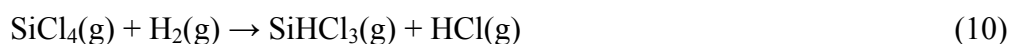
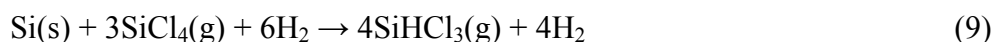
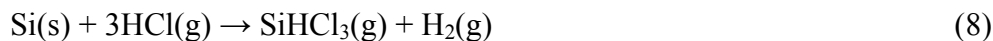


represents a general formula of functional silanes, in which R, R', R'' are organic radicals and X is Cl or OH. There exists a multitude of functional silanes. One of their major applications is as coupling agent between inorganic and organic compounds, for example, inorganic fillers (glass, silica, clays etc.) in organic matrices (epoxy, polyester etc.)

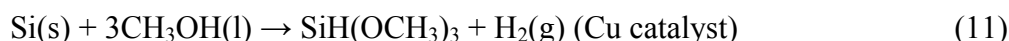
Several routes may be imagined to generate such molecules. The current industrial practice dictated by economics is the functionalisation of trichlorosilane according to



whereas trichlorosilane is produced by a direct synthesis in a fluidized or fixed bed reactor [4]:



A variant recently developed for some classes of functional silanes is the direct synthesis involving silicon and methanol:



Orthoethylsilicate or tetraethoxysilane,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , is an important chemical molecule for glass, ceramic, foundry and painting. It is produced industrially by substitution of Cl in  $\text{SiCl}_4$  or by direct reaction of ethanol with silicon in the presence of a catalyst following the same pattern as (7) and (12) [2 - 4].

The total consumption of silicon metal to functional silanes and orthosilicates may be estimated at 10 000 to 20 000 MT per year.

## 2.3 SEMICONDUCTOR SILICON

Silicon is by far the most important and popular semiconductor material since the emergence of solid-state electronics in the late fifties and the early sixties. Ultra-pure silicon (commercially called *polysilicon*) with the satisfactory semiconductor properties is industrially prepared through the distillation and the thermal decomposition of volatile silicon compounds, for example, trichlorosilane,  $\text{SiHCl}_3$ , and monosilane,  $\text{SiH}_4$ . These operations are performed in large chemical plants, which are sometimes incorporated in plants producing other silicon-based compounds as those described above. Although the ultimate application in the case of polysilicon is in the semiconductor industry, this particular process is, from a silicon raw material perspective, counted among the chemical applications of silicon [2].

The current production of polysilicon in 2000 was approximately 20 000 MT, whereas the installed worldwide capacity was estimated around 25 000 MT. Compared to the other applications of silicon, the use of semiconductor silicon in terms of volume is very modest. However, it is a high-value product. For example, the silicon value is multiplied by a factor of 30 to 50 through upgrading metallurgical grade silicon to polysilicon. This is also the fastest-growing application of silicon with an annual growth rate of approximately 10%, whereas



silicones grows at a 5 to 7% rate, alloys in aluminium at 2 to 3% and silicon metal overall at 4%.

The present raw material for all silicon solar cells originates from this route.

## 2.4 OTHER APPLICATIONS

There are a few other applications of silicon in various fields such as explosives (silicon powder), refractories and advanced ceramics (silicon nitride and carbide). These applications presently do not account for more than 1% of the worldwide silicon metal output.

Because of their anticipated excellent mechanical and chemical resistance properties, alloys rich in silicon should have a bright future. They may be prepared by powder metallurgy, mixing and sintering silicon powder with metallic powders (e.g. Cu, Al, Ti, Co, V etc.) [5].

The present publication does not review the applications of silicon, such as silica in glasses, ferroalloys and silicon carbide, in which silicon is usually added to the production process as natural silicate, quartz, quartzite or silicon alloys.

## 3 PRODUCTION OF METALLURGICAL GRADE SILICON

### 3.1 THE CARBOTHERMIC REDUCTION OF SILICA

Metallurgical grade silicon, also called *silicon metal*, with a typical purity of 98.5% Si is produced in submerged electric arc furnaces. In principle, this process is much the same as it was at the beginning of the twentieth (XX) century when it was first developed for ferrosilicon and other alloys. However, practice has greatly improved with larger furnaces, more efficient material handling and improved control of the operations. This has led to a continuous decrease of the specific energy consumption.

The electric furnace consists essentially of a vessel filled with quartz and carbon materials. Silicon is freed by the carbothermic reduction of silica according to the overall reaction:



Contrary to what is often claimed in popular articles or reviews, silica sand is currently not used for this purpose. Lumpy quartz (e.g. 10–100 mm) with appropriate purity and thermal resistance is preferred. Carbon raw material generally consists of metallurgical grade coal as well as woodchips and/or charcoal and coke. Raw materials, both quartz and carbon, are selected in order to achieve high product quality (silicon and silica fumes), to maximize

furnace performances and to minimize the environmental damages (i.e. SO<sub>2</sub> and NO<sub>x</sub> emissions) [2]. The raw material reactivity and the consistency of the mix of raw materials in the charge, for instance its porosity, are extremely important factors in achieving good furnace performance in terms of high material yield, lower power consumption and good product quality.

The raw material mix or charge is heated by means of an intense electric arc sustained between the tips of three submerged electrodes and the electrical ground of the furnace. Although important exceptions exist, the current practice is to run this process in a three-phase current, open and rotating furnace at a working electrical load normally between 10 and 30 MW, depending on the size of the furnace. The tendency is to increase the furnace size and the electrical load in order to achieve higher output and productivity.

Electrodes are also made of carbon. The electrode technology is an important aspect of the present development of this industry: half a dozen electrode types ranging from pre-baked to self-baking electrodes of Söderberg type are currently used or are in the process of development.

Liquid silicon metal is tapped from the bottom of the furnace, and the thoroughly mixed raw materials are charged on the top.

To understand the processes occurring in the furnace, it is convenient to conceptually split the furnace reaction inner space into an inner hot zone and an outer cooler zone. Liquid silicon is produced in the inner zone, where the dominant chemistry is described by the reactions



The temperature in the inner zone is in the range of 1900 to 2100°C, allowing a high proportion of SiO(g) in this zone, which is indispensable for further reduction according to reaction (17).

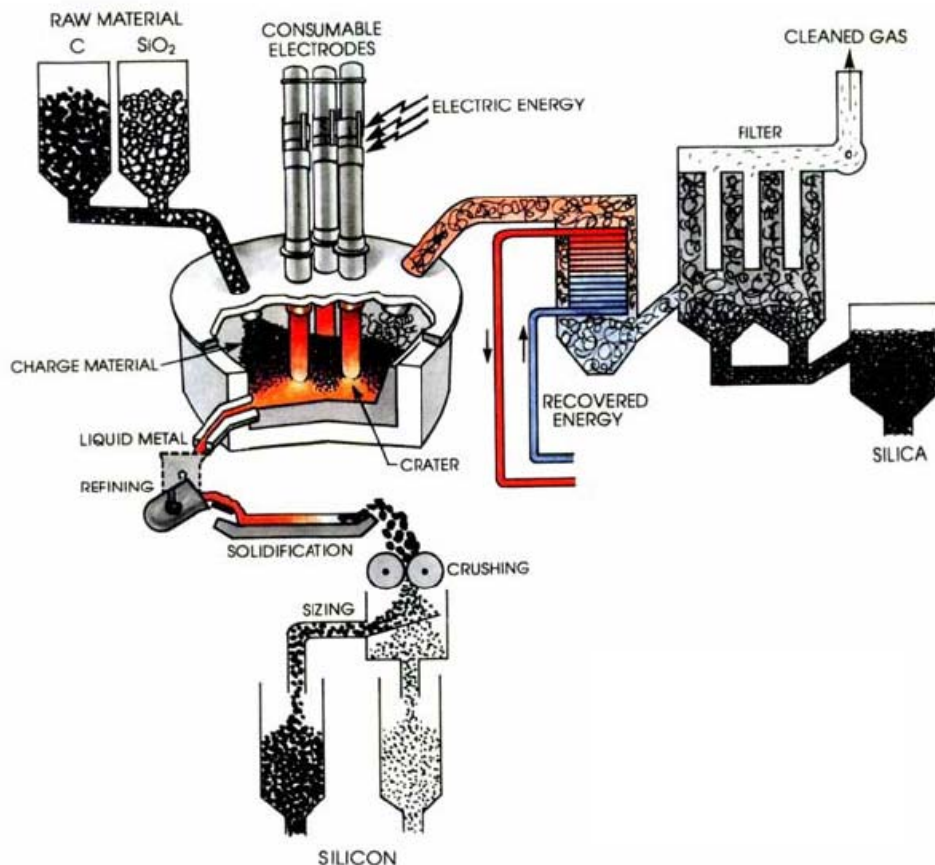
In the outer zone, where the temperature is below 1900°C, SiO(g) and CO(g) coming from the inner zone meet and react with free carbon. Consequently, silicon carbide SiC(s) and condensation products of Si(l) in a matrix of SiO<sub>2</sub>(s,l) are formed as the partial pressure of SiO(g) drops:



A schematic description of the furnace is given in Figure 1.

The high-temperature nature of this process implies operation as continuous as possible. Raw materials are therefore fed in small batches with frequent intervals and are judiciously distributed on the top of the charge. Liquid silicon is at frequent intervals, drained out from the bottom of the furnace, whereas gas exhaust and fumes are constantly passing through the filter to clean the fumes and recapture the silica.

The silica fumes, which consist mainly of very fine particles of amorphous silica less than  $1\ \mu\text{m}$ , are passed through filter cloths installed in large bag-house systems adjacent to the furnaces. The collected amorphous finely divided silica finds valuable applications as additives in concrete and refractory. Depending on the quality of the raw materials used and the operational strategy and skills, the silicon yield as metallurgical silicon ranges from 80 to 90%, the balance resulting in silica fume [2].



**Figure 1:** Schematic representation of a furnace for production of metallurgical grade silicon. Reproduced from Schei A, Tuset J, Tveit H, *Production of High Silicon Alloys*, Tapir forlag, Trondheim (1998).

Liquid crude silicon contains 1 to 3% impurities depending on the raw materials and the type of electrodes. The main impurities are

Fe: 0.2–1%

Al: 0.4–0.7%

Ca: 0.2–0.6%

Ti: 0.1–0.02%

C: 0.1–0.15%

### 3.2 REFINING

Most of the applications of silicon as described above require further refining. The crude silicon is therefore tapped as liquid in large ladles (containing up to 10 MT of silicon) and treated when still liquid with oxidative gas and slag-forming additives, mainly silica sand ( $\text{SiO}_2$ ) and lime/limestone ( $\text{CaO}/\text{CaCO}_3$ ). Other chemicals such as dolomite ( $\text{CaO-MgO}$ ), calcium fluoride ( $\text{CaF}_2$ ) and others are used depending on plant practice and customer requirements. Elements less noble than silicon such as Al, Ca and Mg are oxidized and the degree of refining is determined by distribution equilibriums (20) to (23), where the (parentheses) refer to components dissolved in a slag phase and the underscored symbols refer to dissolved elements in liquid silicon:



Theoretically it is possible to remove Al and Ca to very low levels, but in practice this is prevented by the large heat losses occurring during this operation. Temperature drops from 1700 to 1500°C, and to avoid freezing of the melt, some of the silica needed for slag formation is provided by direct oxidation of Si(l) in order to heat silicon to keep it liquid. A disadvantage of this operation is the loss of silicon [6].

After completion of oxidative refining in the ladle, the slag, which contains part of the impurities, is removed mechanically or by gravity and liquid silicon is poured into a casting mold. The slag-forming additives influence the slag density and viscosity, hence the practical separation of slag and the ultimate purity of the poured silicon. Sufficiently different properties in density and viscosity of both the slag and the molten silicon are required to achieve a good separation. Many studies and practical on-site developments have been devoted to this step of the process [5, 6].

Carbon is present in crude liquid silicon mainly as dissolved C and suspended SiC particles. The fraction of SiC increases as the temperature is lowered; SiC particles are then captured by the slag phase and thus are removed from liquid silicon during the ladle treatment and the subsequent pouring. SiC is also removed simply by mechanical separation, precipitated particles sticking to the walls of the ladle and the other devices containing the liquid silicon. Dissolved carbon in the range of 80 to 100 ppm(m) in best cases will finally remain in the purified alloy of metallurgical silicon.

The use of these refining principles to prepare solar grade silicon will be further discussed.

## **4 PRODUCTION OF SEMICONDUCTOR GRADE SILICON (POLYSILICON)**

Impurities in the ppb(a)–ppt(a) range are required for polysilicon supplied to the semiconductor industry. The ultra-high purity is needed to ensure exacting semiconductor properties in the grown silicon crystals. This is achieved first by the preparation of a volatile silicon hydride and its purification generally using fractional distillation. This is followed by the decomposition of this hydride to hyper pure elemental silicon by reductive pyrolysis or chemical vapor deposition. The preparation of the volatile Si compound involves external reactants and its decomposition generates by-products, which need to be recycled. The various polysilicon routes therefore must control four successive steps [2; 4]. All have a strong impact on the overall feasibility and economics of the suitable polysilicon products:

1. preparation/synthesis of the volatile silicon hydride
2. purification
3. decomposition to elemental silicon
4. recycling of by-products.

Many processes to produce polysilicon have been tested, patented and a few operated for many years. Only three large commercial processes are currently active:

1. The most popular process is based on the thermal decomposition of trichlorosilane at 1100°C on a heated silicon rod placed inside a deposition chamber. This process, which was developed in the late fifties, is commonly referred to as the Siemens process with reference to the company that carried out its early development.



In 2001 this process still accounted for at least 60% of the worldwide production of polysilicon.

2. In a more recent process developed by Union Carbide Chemicals in the United States of America, the trichlorosilane has been replaced by monosilane  $\text{SiH}_4$ , but the principle of decomposition on a heated silicon rod inside a closed deposition chamber is maintained.



This process, presently run by the company *Advanced Silicon Materials, LLC*. has gained during the past 15 years a significant market acceptance.

3. Finally, in the third process, also making use of monosilane  $\text{SiH}_4$ , the heated silicon rod in the closed reaction chamber has been replaced by a heated fluidized bed containing silicon particles. The particles act as seeds on which  $\text{SiH}_4$  is continuously decomposed to larger granules of hyper-pure silicon. Unlike (1) and (2) this process is a continuous one. This process is known as the Ethyl Corporation process, after the name of the US chemical company that developed it. This process is presently run by the US corporation MEMC in Pasadena, Texas.

The respective features, advantages and disadvantages of these different routes are described in the following sections.

#### 4.1 THE SIEMENS PROCESS

Trichlorosilane  $\text{HSiCl}_3$  is prepared by hydrochlorination of metallurgical grade silicon in a fluidised bed reactor [1, 2, 4]:



This reaction occurs at 350°C normally without a catalyst. A competing reaction is

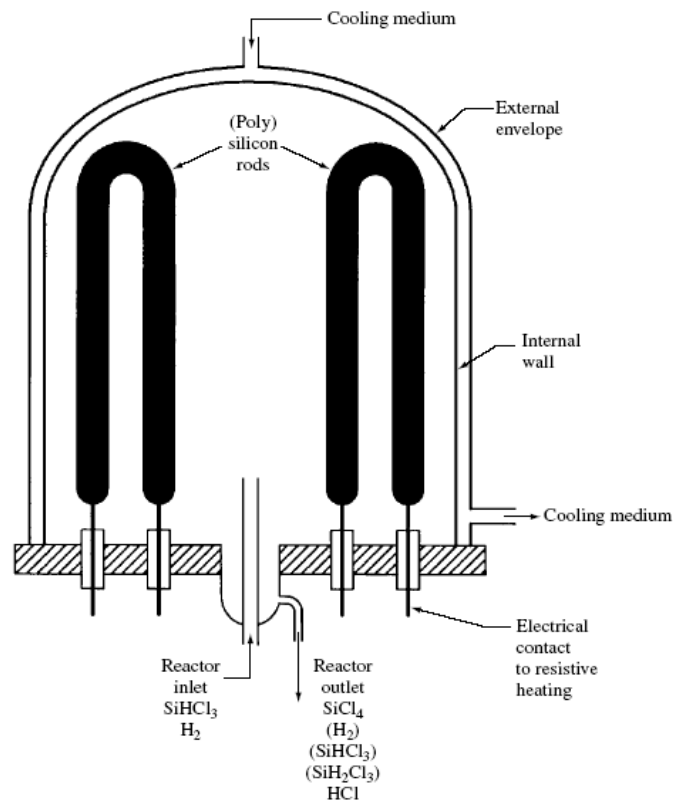


contributing to the formation of unsuitable tetrachlorosilane in molar proportion of 10 to 20%. Trichlorosilane is chosen because of its high deposition rate, its low boiling point (31.8°C) and its comparatively high volatility and hence the ease of purification with respect to boron and phosphorus down to the ppb level. The suitable trichlorosilane undergoes a double purification through fractional distillation, the first step removing the heaviest components resulting from the direct synthesis and the second step eliminating the components lighter than trichlorosilane, also called *volatiles*. High-purity  $\text{SiHCl}_3$  is then vaporised, diluted with high-purity hydrogen and introduced into the deposition reactors. The gas is decomposed onto

the surface of heated silicon seed rods, electrically heated to about 1100°C, and growing large rods of hyperpure silicon. The main reactions are:



The stream of reaction by-products, which leaves the reactor, contains H<sub>2</sub>, HCl, SiHCl<sub>3</sub>, SiCl<sub>4</sub> and SiH<sub>2</sub>Cl<sub>2</sub>.



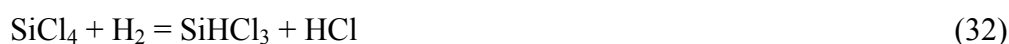
**Figure 2:** Schematic representation of the traditional Siemens reactor

A schematic representation of the Siemens reactor is given in Figure 2. The Siemens process is highly energy consuming, a major part of the energy being dispersed and lost. To avoid deposition on the inner surfaces of the reaction chamber, they have to be cooled. The decomposition chamber consists of a steel bell jar where 30 or more inverted U-rods are placed in each reactor [2].

As reactions and equilibriums (28) to (31) show, the deposition process generates by-products. Unfortunately, for each mole of Si converted to polysilicon, 3 to 4 moles are converted to SiCl<sub>4</sub>, binding large amounts of chlorine and valuable silicon. The main

industrial application of tetrachlorosilane is as a source material to produce pyrogenic (also called *fumed*) silica as described above in this chapter. The present market of fumed silica is about 60 000 MT measured in terms of silicon unit. This presently corresponds to three times the output of polysilicon in 2000. Moreover, a significant portion of fumed silica is also produced by burning derivated by-products from the silicones industry. In the early stages of the polysilicon industry, the fumed silica business could absorb the excess of silicon tetrachloride generated by the Siemens process. This explains the arrangements between polysilicon and fumed silica producers all around the world. With polysilicon production growing much faster than silicones and fumed silica, the question was whether to eliminate or recycle the tetrachlorosilane. This became an environmental and economical necessity. The concept of recycling on site the by-product back to the valuable starting material to form a closed-loop production process is generally an ideal preferred solution. There are two basic chemical processes applicable to reconvert  $\text{SiCl}_4$  to  $\text{SiHCl}_3$ :

1. The high temperature reduction of silicon tetrachloride with hydrogen.



At about 1000°C, a 1:1 molar mixture of  $\text{SiCl}_4$  and  $\text{H}_2$  produces approximately 20 to 25% molar  $\text{SiHCl}_3$  in the gaseous mixture. This process requires a fair amount of electrical energy but has a distinct advantage that the trichlorosilane produced is of very high quality because both reactants, silicon tetrachloride and hydrogen, are basically electronic grade when produced by equations (28) and (31).

2. The hydrogenation of silicon tetrachloride in a mass bed of metallurgical silicon.



This hydrogenation reaction produces approximately 20% trichlorosilane at 500°C and 35 bar with a 1:1 ratio of  $\text{SiCl}_4$  to  $\text{H}_2$  in one pass through metallurgical grade silicon in a fluidized bed reactor. In spite of its widespread and dominant position in the industry, the Siemens process as described above suffers from the following disadvantages:

- High energy consumption, over 90% of the input power is lost to the cold walls of the reactor.
- Two power supplies and preheating of the seed rods are normally required because the high-resistivity (~230 000 ohm cm) seed rods require very high power supplies and high initial power rates to heat the rods. Therefore, a separate power supply for quartz lamps or graphite rod induction heating is used to preheat seed rods to about 400°C (~0.1 ohm cm). Lower power electrical supplies can then be used to provide continued heating and control.



- Electrical contacts to seed rods are made of graphite, which is a source of contamination.
- Power failure (especially when starting the process) causes run abortion.
- Hot spot formation and filament burn out may occur.
- Problems arise owing to gas inclusions and to non-uniform deposition at the joints.
- Gas flows and electrical power have to be adjusted during the process to obtain optimal deposition rate.
- The process is operated batchwise.

Large amount of by-products need to be handled or recycled.

More recent processes have attempted to overcome some of these disadvantages.

## 4.2 THE UNION CARBIDE PROCESS

The main steps for the union carbide process are as follows:

The hydrogenation of tetrachlorosilane through a mass bed of silicon metal is carried out in a fluidised bed reactor as already described by equation (33).

The trichlorosilane is separated by distillation while the unreacted tetrachlorosilane is recycled back to the hydrogenation reactor.

The purified trichlorosilane is then treated in two separate steps through fixed bed columns filled with quarternary ammonium ion exchange resins acting as catalyst to.



Products of (34) and (35) are separated by distillation. Tetrachlorosilane and trichlorosilane are recycled to the hydrogenation (33) reactor and the first step (34), respectively. Silane is further purified by distillation and then pyrolysed to produce polysilicon onto heated silicon seed rods mounted in a metal bell-jar reactor:



With hydrogen and chlorine recycled, the only raw material requirement is metallurgical grade silicon in granular form designed for fluidisation. Since equations (33) to (35) yield low fractions of suitable products, and the intermediates tri- and tetrachlorosilane are distilled, recycled and purified many times before conversion to silane. This results in an extremely high purity for the silane and the subsequent polysilicon. It is operated as a closed-loop process [2].

Advantages of using  $\text{SiH}_4$  are that the pyrolysis may be operated at significantly lower temperature, the decomposition is complete, conversion efficiency is higher and no corrosive

compounds are formed. Uniform, large-diameter, long, dense, void-free cylindrical rods of polysilicon produced this way are particularly suitable for single-crystal manufacturing by the floating zone (FZ) method.

The disadvantage of the monosilane-based process is the high cost since additional steps are required to convert trichlorosilane to monosilane. Each recycling of unsuitable chlorosilanes yields only a small percentage of the suitable silane.

### 4.3 THE ETHYL CORPORATION PROCESS

The Ethyl Corporation process is, by comparison with the Siemens and the Union Carbide processes, revolutionary in all aspects except for the concept of purifying and decomposing a volatile silicon compound by pyrolysis.

The first radical change was the choice not to use metallurgical grade silicon as the primary raw material for silane. The idea was to make use of silicon fluoride, which is a waste by-product of the huge fertilizer industry. Tens of thousands of tones of silicon fluoride every year are available. This is potentially a very low-cost starting material. Silicon fluoride is hydrogenated to monosilane by metal hydrides such as lithium aluminium hydride or sodium aluminium hydride.

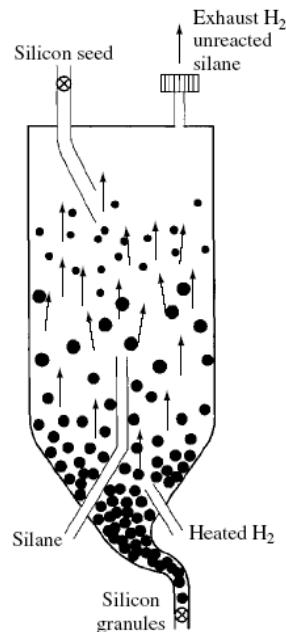


$\text{AlMF}_4$  is believed to find application in the aluminium industry, making it a valuable saleable product.

After distillation, monosilane  $\text{SiH}_4$  is thermally decomposed to polysilicon as described by (36). However, to realize this process, Ethyl Corporation introduced a second radical change, not using static silicon seed rods in a bell-jar reactor but dynamic silicon seed spheres in a fluidised bed sustained by a gas stream of silane and hydrogen. A schematic representation of a fluidised bed reactor is given in Figure 3.

The fluidised bed reactor offers significant advantages compared to the bell-jar reactor. Most of the shortcomings identified for the Siemens process are then eliminated. The energy losses and hence the energy consumption are considerably reduced because the decomposition takes place at a lower temperature and because the requirement to cool the bell jar is not there. Another advantage is that large reactors may be constructed and operated continuously, reducing further the capital and operating costs [4].

The end products are small granules of polysilicon that may present some advantages (e.g. when continuous feeding in customer process is requested) or disadvantages (e.g. not usable for direct float zone crystallisation).



**Figure 3:** A schematic representation of a fluidized bed reactor for polysilicon production

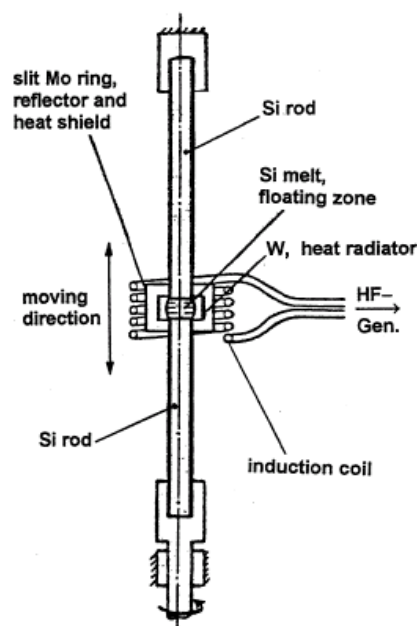
A disadvantage of the process is the generation of powder due to homogeneous decomposition of  $\text{SiH}_4$  in the free reactor space and the hydrogen absorption into the polysilicon deposition layer.

#### **4.4 CRUCIBLE-FREE ZONE REFINING, FLOAT ZONE SINGLE CRYSTAL GROWTH**

Since 1951, Pfann has developed and investigated the zone refining of germanium in a strongly elongated boat crucible made from graphite or silica glass [8]. The boat was first filled with granulated germanium. By passing a short melt zone from one end of the crucible to the other, a large part of the impurities of the germanium were driven by segregation to the end where the melt froze finally. This could be repeated several times and the germanium got purer and purer. With zone refining, most of the unwanted impurities can be reduced strongly, but not all. Boron in silicon, for example, cannot be reduced sufficiently. The zone refining works only for impurities with small effective partition ratios. For very low boron concentrations in silicon, other methods like distillation of silanes must be applied. By placing a seed crystal at the starting end of the boat, the growth of germanium single crystal is also

possible, but not that of silicon single crystals. Liquid silicon reacts too strongly with the crucible material and becomes polycrystalline [7].

To also apply zone refining to silicon, several researchers simultaneously started in 1952 to develop or to invent, respectively, the crucible-free zone refining of silicon and, later on, the crucible-free pulling of silicon single crystals. Fig. 3 shows the float zone growth arrangement of Emeis [10]. With these arrangements, both float zone refining and float zone single-crystal growth could be realized. Because they first did not use seed crystals, the orientations of the grown crystals were accidental. However, most of the single crystals showed  $\langle 111 \rangle$  orientation, because this is the most stable and slowest growing interface. The main difference between the different growth methods that were developed was the heating technique. Theuerer [9] used a lateral resistance heater made of graphite, which heated the silicon by heat radiation. Emeis also used heat radiation for melting, but his heat radiator was a circular tungsten sheet that was heated from outside by an induction coil.



**Figure 4:** FZ melting according to Emeis for the zone refining and single-crystal growth of silicon from the year 1953.

For float zone growth, it was necessary to have the starting silicon in the form of a stable rod, which should have about the same diameter as the crystal to be grown. At the Bell Laboratories, 320 g ingots of 1.75'' diameter and 5'' length of already rather pure polycrystalline silicon, grown according to the technique of Scaff et al. [11], were taken and machined to small rods of 0.25'' diameter. These small rods were used at first by Theuerer in his float zone refining and single-crystal growth apparatus described in his patent [16]. At

about the same time, at Siemens, Ziegler developed the sintering of rods from silicon powder, which was produced by chemical vapor deposition from trichlorosilane  $\text{SiHCl}_3$  and hydrogen according to reaction (39):



for the float zone refining and single-crystal growth experiments of Emeis [10].

## **5 PURIFICATION OF METALLURGICAL GRADE SILICON BY ACID LEACHING**

Many metallic elements such as Fe, Al, Mg, Sb, Sn, Zn, Cu, Au, Ni and Ti have low effective partition ratios in silicon. These elements are highly soluble in molten silicon but their solubilities in solid silicon are relatively low. Thus, during solidification of molten MG-Si, a major portion of the less soluble impurities precipitate at grain boundaries or at interstitial positions in polycrystalline silicon [13].

The individual Si grains vary in size typically from 1 mm close to the iron mold wall to up to more than 100 mm in the centre section if cast on a bed of silicon fines [12]. The impurities are generally located at the Si grain boundaries as silicides and intermetallic compounds, but may also be incorporated in the Si grains if solidification has been sufficiently rapid. Oxides and carbides are found as inclusions located at the grain boundaries and to a lesser degree inside the Si grains. When the cast MG-Si is pulverized, breakage occurs mostly at grain boundaries. Thus if MG-Si lumps are pulverized to a particle size equivalent to the size of the polycrystalline grains, a major portion of the metallic impurities present on the surface of the grains is exposed. These precipitates dissolve fairly well in acids, therefore prolonged treatment of pulverized MG-Si with acids should be effective in removing these impurities.

Crushing of solidified silicon is performed in jaw crushers and roll crushers because at room temperature metallurgical grade silicon is hard and brittle. This operation generally generates significant amount of fines, which are undesirable because they may be contaminated by impurities and are difficult to handle during further transport and handling. Therefore, fines are removed after the primary crushing. For chemical applications, silicon lumps need to be further reduced to small powder particles of a few tens to a few hundreds of micrometers. This is carried out in industrial equipment such as ball mills. Alternative

methods based on rapid cooling have recently been developed to increase the homogeneity of the solidified structure of silicon through an even distribution [14].

The acid leaching process for purifying MG-Si has been reported by Voos [15], Hunt et al. [16] and Chu [17], and by different companies in silicon production e.g. Elkem, Union Carbide, Alcoa, Heliotronic, Siemens and others. Of these, only the Elkem process is in regular industrial operation. Voos patented a process for treating pulverised MG-Si with aqua regia,  $H_2SO_4$ , HF, etc., to yield silicon suitable for application in microwave diodes. Hunt et al. [2] reported that over 90% of the impurities present in MG-Si could be removed by etching MG-Si particles of less than 500  $\mu m$  size with aqua regia for 12 h at 75°C. Chu [17] carried out detailed studies on the partial purification of MG-Si by refluxing with aqua regia, HCl and a mixture of  $H_2SO_4$  and  $HNO_3$ . Leaching MG-Si with aqua regia for long periods was found to be the most effective. However, the investigators recommended leaching under high pressure and temperature conditions to achieve faster leaching rates.

The acid treatment or leaching methods are not effective in removing interstitial and substitution impurities such as boron, carbon and oxygen. Adding Ca to the silicon alloy prior to acid treatment, however, shows that P could be reduced by a factor of 5 down to a concentration less than 5 ppm(m), probably because P is dissolved in calciumsilicide [13]. Adding barium also proves to have some effect on boron dissolution.

## **6 PURIFICATION OF METALLURGICAL GRADE SILICON BY ALLOYING PROCESS**

The alloying process for purification of MG-Si is based on the principle of fractional crystallization. In this process MG-Si is melted in the presence of a solvent metal which is miscible with silicon in the liquid state, but immiscible in the solid state. Metals which can be used for alloying include Mg, Al, Sb, Sn, Zn and Cu. During the melting process, the impurities present in MG-Si are distributed between the solvent and solute phases according to their distribution coefficients. During solidification of the molten alloy, pure silicon crystallizes out and a major portion of the impurity elements such as Fe, Al, Cu, Au, Ni and Ti which have low solubilities in solid silicon are either retained in the solvent or are deposited at the grain boundaries of the alloy. Pure silicon crystals are separated from the solvent metal either by electrochemical dissolution or by pyrometallurgical processes such as

high temperature distillation of the latter. In some cases, acid leaching of the metal-silicon alloy can be employed for removing the solvent metal.

The purification of MG-Si by the alloying process has been used by Driole and Bonnier [18] who alloyed crude silicon with antimony or tin and then removed the solvent metal by distillation. The pure silicon crystals were made free of segregated impurities by final treatment with acids. Purification by this route however has the disadvantage that most of the impurities are left behind along with silicon in the residue and have to be removed by acid treatment. Obinata and Komatsu [19] employed aluminium as the solvent metal for purifying crude silicon. The process was later improved later by Juneja and Mukherjee [13] who recommended the use of magnesium and copper as the solvent metals. In the aluminium and magnesium alloying processes, silicon normally became contaminated with oxides of aluminium and magnesium which did not respond to separation by acid leaching. In this respect, the copper refining process was considered superior as copper or its oxides present in silicon could be easily removed by acid leaching. However, the quantitative results of purification achieved in different stages of the copper alloying process, were not reported. Among the different alloying agents, copper appears to be attractive because of the following considerations: (i) the solid solubility of copper in silicon is negligible; (ii) copper can be easily recovered for reuse by aqueous electrolysis; (iii) even if oxides of copper form during purification, they can be removed from the anode slime by acid treatment (with aqua regia and HF). Juneja and Mukherjee [13] suggested that copper alloying process can be followed by electrolytic removal of copper.

## **6.1 BORON AND PHOSPHORUS REMOVAL BY SOLIDIFICATION WITH SI-AL MELTS**

Yoshikawa *et al.* [20, 21] studied boron removal from Si-Al melts. Boron forms a thermodynamically stable compound,  $TiB_2$ , if titanium is added to melt. Addition of excess Ti to the Si-Al melt will not be harmful because it forms acid-leachable  $Al_3Ti$  and  $Si_3Ti$  solid solutions during cooling. These precipitates  $(Al, Si)_3Ti$  and  $TiB_2$  are mostly embedded in the Al-Si eutectics and are dissolved during the acid leaching process together with the Al-Si eutectics. The results show that the B content of refined Si is reduced to several ppma and the removal fraction of B from Si by solidification refining would be larger than 90%. An initial content of 280 ppma B and 1105 ppma Ti in the Si-Al melt before solidification resulted in 10 ppma B and 978 ppma Ti in the solid silicon after leaching. However, further treatment for B removal is necessary to achieve a low-cost Si refining process [22].

Phosphorus removal by alloying process of silicon with aluminum has been studied too [22, 23]. The calculated partition ratios of phosphorus at its infinite dilution at 1173 – 1373 K indicate the strong affinity between phosphorus and aluminum in solid silicon. Phosphorus contents of the liquid Si–Al alloys is equilibrated with AlP which can be removed effectively by solidification refining process with the Si–Al melts such as zone melting or directional solidification [22].

A thermodynamic study on interaction parameters of calcium and phosphorus in molten silicon is reported by Shimpo *et al.* [23]. According to this study calcium has a strong affinity for phosphorus which results in decreasing the activity coefficient of phosphorus in molten silicon, and, thereby, reduces partition ratios of phosphorus in silicon. Moreover, phosphorus, which condenses in the secondary precipitate mainly composed of  $\text{CaSi}_2$ , may also be removed together with iron and titanium by an acid leaching treatment. Removal fraction of phosphorus from silicon with calcium addition is about 80 % when 5.17 at% calcium is added.

## **7 REFINING OF MULTICRYSTALLINE SILICON BY DIRECTIONAL SOLIDIFICATION**

The efficiency of the crystallisation processes may be predicted by the effective partition ratios of each impurity element between the solid and the liquid silicon phases. Published data clearly show that N, Ti, Cr, Fe, Co, Ni, Cu, Zn have ratios in range  $10^{-4} - 10^{-6}$  indicating that solidification process has a large purifying effect for these elements. But, the elements belonging to the Group IIIA (B, Al, Ga) and the Group VA (P, As, Sb) have a ratio close to 1, making it difficult to separate them from the silicon [24].

Various methods have been claimed to be useful for refining silicon by directional solidification resulting in large oriented crystals while the Bridgman and the block-casting processes are the main employed. In both processes the solidification of high-quality multicrystalline silicon ingots with mass of 250 to 300 kg, dimensions of up to  $70 \times 70 \text{ cm}^2$  and heights of more than 30 cm have been successfully realized.

The main difference between both the techniques is that in the Bridgman process only one crucible is used for both melting and crystallization, whereas in the block-casting process



two different crucibles are used, one for the melting process and the other for solidification process.

In the case of the Bridgman process, a silicon nitride ( $\text{Si}_3\text{N}_4$ )-coated quartz crucible is usually employed for melting of the silicon raw material and subsequent solidification of the multicrystalline ingot. The  $\text{Si}_3\text{N}_4$  coating thereby serves as an anti-sticking layer preventing the adhesion of the silicon ingot to the quartz crucible walls. Owing to the volume expansion during crystallisation of the silicon material, a destruction of both the silicon ingot and the crucible would take place. In the block-casting process, melting is performed in a quartz crucible without a coating, whereas – after pouring the molten silicon into a second crucible – for the crystallisation also a  $\text{Si}_3\text{N}_4$ -coated one is used [24].

Usually, in both production technologies, crystallisation starts at the bottom of the crucible by lowering the temperature below the melting temperature ( $1410^\circ\text{C}$ ) of silicon. In the Bridgman [24, 25] process the temperature reduction is achieved by simply lowering the liquid silicon-containing crucible out of the hot area of the crystallisation furnace. In the block-casting process the temperature control is achieved by an adjustment of the heaters, whereas the crucible itself is not moved during solidification.

After solidification starts in the bottom region, the crystallisation front, that is the liquid–solid interphase, moves in a vertical direction upwards through the crystallization crucible. This so-called directional solidification results in a columnar crystal growth. Adjacent wafers fabricated out of the ingots show nearly identical defect structures (grain boundaries and dislocations).

Common crystallisation velocities used for the Bridgman technology are in a range of about 1 cm/h (corresponding to a mass of approximately 10 kg/h for large ingots). Allowed cooling rates of the already crystallised fraction of the ingot determines productivity. Too high solidification rates cause large thermal gradients within the solidified silicon that may result in cracks or even destruction of the ingot. For the block-casting technology, however, owing to the more versatile and sophisticated heater system, considerably higher rates can be achieved [25].

## **7.1 RECYCLING OF TOP-CUT SILICON SCRAP FROM INGOTS**

After directional solidification in the Bridgman and block-casting processes, the regions showing presence of solid particles are cut off from the ingot. Usually 10-20 mm is cut off from the sides of the ingot. The cut regions have a maximum concentration of impurities since the impurities with low partition ratios are present in high levels in the top of

the cast ingot, and the concentration of impurities with high ratios is high in the bottom of the ingot. As a result the top of the ingot is highly contaminated with impurities such as SiC, Si<sub>3</sub>N<sub>4</sub>, boron, phosphor, iron, aluminum, etc. While the bottom and sides are recycled and used again in the solidification process, the top-cut is sold as scrap to the steel industry. A considerable amount of silicon is lost this way from. Making it possible to recycle silicon scrap would reduce the cost of solar cells [26, 27].

Work on recycling top-cut silicon scrap by filtration has been performed recently. The technology of filtration is established in the aluminium and steel industries to remove harmful inclusions. Top-cut silicon scrap is melted in a high vacuum furnace at around 1500°C. The filters, from commercial producers, are C and SiC with 10, 20 and 30 ppi (pores per inch). Filtration with such ceramic foam filters has proved to be very efficient (around 97 %) for removal of SiC and Si<sub>3</sub>N<sub>4</sub>. Almost all inclusions larger than 10 µm can be removed through this technique. Si<sub>3</sub>N<sub>4</sub> particles are mainly found on the top surface of the filter, a process named “cake filtration”, while SiC particles are mainly removed by entering the pores and attaching to the filter material, called “deep bed filtration” [27].

## **8 PRODUCTION OF SOLAR GRADE (SOG) SILICON BY REFINING LIQUID METALLURGICAL GRADE (MG) SILICON**

As mentioned, most of the impurities can be removed by directional solidification as most impurities have a low partition ratio in silicon. The problematic elements are B and P, which cannot be removed effectively from silicon by directional solidification. Therefore, while directional solidification from the molten state has to be a key refining step, it is necessary to develop additional refining procedures focused on removing B and P from molten silicon prior to directional solidification. It is desirable that all impurities including B and P be reduced from MG silicon as much as possible prior to directional solidification to yield a high amount of SoG silicon. In view of these features, emphasis is placed on the refining procedures and evaluating their effects on all impurities in MG silicon.

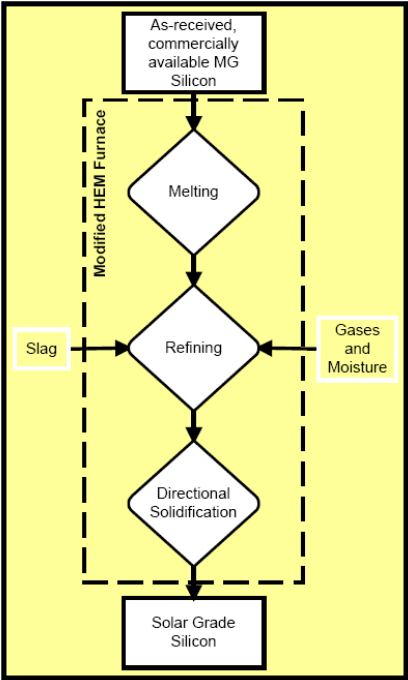
A cooperative effort between Exxon and Elkem indicates that it is possible to upgrade MG silicon in the arc furnace and use it as feedstock for photovoltaic applications. Several approaches to upgrade MG silicon in an arc furnace were pursued in Germany, but these

efforts were stopped before commercialization. Similarly, other approaches did not result in a product.

Programs to upgrade MG silicon have also been carried out in Japan. Work in Japan has shown that it is possible to upgrade MG silicon for photovoltaic applications, and Kawasaki Steel Corporation set up a pilot production facility to demonstrate the full process under funding from NEDO [30]. In this process, a high purity MG silicon is treated under vacuum to remove P, followed by reduction in Al and Fe levels by a first directional solidification step. Boron is removed from the surface by reaction with Ar plasma and water vapor, and finally a second directional solidification produces SoG silicon. Laboratory results are encouraging with respect to reducing impurities, but vacuum processing, two directional solidifications and treatments in Ar plasma make it difficult to produce SoG cost effectively.

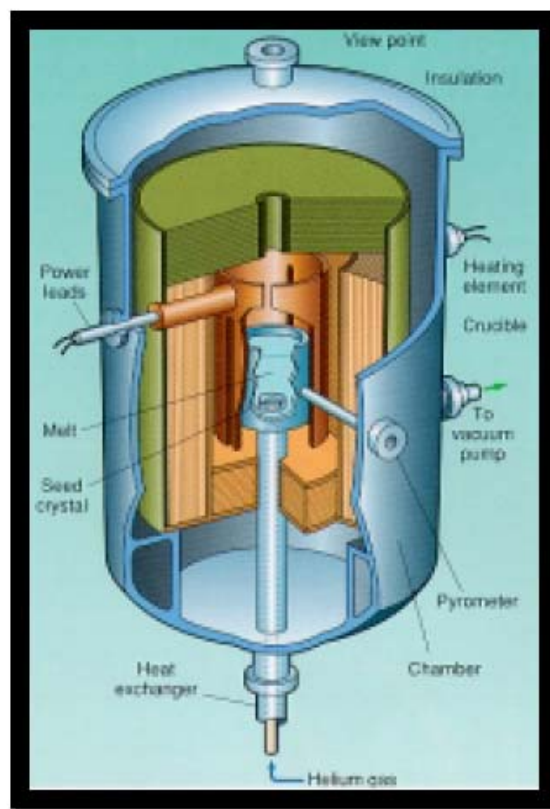
Several simple refining procedures to upgrade molten MG silicon and follow the refining step by directional solidification are presented. The approach, developed from Khatak, Joice and Schmid, is different from that of Elkem and Kawasaki. However, it includes the essential components of both these approaches and is based on laboratory results which have shown that each of the impurities in MG silicon can be reduced to less than 1 ppm level (including B and P) [28].

A schematic approach for the refining process is shown in Figure 4.



**Figure 4:** A schematic of the approach to upgrade MG silicon to SoG silicon using a modified HEM furnace [28].

All these processes are performed in the large Heat Exchanger Method (HEM) furnace which has the necessary features for the refining processes. The standard HEM furnace has the built-in features of good vacuum capability, one of the best directional solidification systems, a heat zone designed for silicon processing, and capability to use vacuum or controlled atmosphere. A schematic of the HEM furnace is shown in Figure 5. The furnace is designed for commercial production of 69-cm square cross section silicon ingots. This means that the same furnace can be used if the size of the ingot is increased. To accommodate the larger sizes, a round fused silica crucible is employed allowing production of up to 450 kg charges [29].



**Figure 5:** Schematic of an HEM furnace [29].

## 8.1 EVACUATION

The simplest refining step is to remove volatile elements from MG silicon by heating MG silicon in a molten stage under vacuum. A major advantage of this refining step is that the impurities (and their residual effects) are removed from the MG silicon. Vacuum processing of molten silicon has been shown to be effective for reducing P concentration in silicon, as well as Na, Mg and volatile elements such as, S and Cl.

## 8.2 FORMATION OF VOLATILE SPECIES

If the impurity elements can react to form volatile molecular species, further refining can be achieved. Some of the elements that can be removed through the vapor phase by complexing with O, H and/or Cl include Li, B, Mg, Al, P, Fe, Co etc. Volatile products of impurities can be formed by reaction with solid powders or gases. The solid powders can be added to the initial charge of MG silicon prior to melting or to the molten charge with a reactive gas [29].

## 8.3 OXIDATION OF IMPURITIES

Impurity elements in MG silicon can be oxidized to form other species and separated from MG silicon in a slag. In this case, the species formed has to be more stable than the elements remaining in MG silicon.

For example, B in Si (l) can react with H(g) and SiO(g) to form HBO(g); B forms HBO and is removed to the vapor phase



In addition to the vapor, the impurity species can also partition into a liquid phase such as a slag, or into a solid phase such as Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub>.

A large number of species used in the vapor phase removal calculation is considered for refining of impurities among which Ar(g), H<sub>2</sub>O(g), H(g), H<sub>2</sub>(g), HBO(g), HBO<sub>2</sub>(g), P(g), P<sub>2</sub>(g), PH(g), PO(g), Si(g) and SiO(g), are stable. Preliminary analysis of the thermodynamics of the process indicates that the observed removal of B and P during steam blowing cannot be explained in terms of reduced B and P species volatilities. Under equilibrium conditions, less B and P are partitioned to the vapor phase than in liquid silicon, resulting in increasing concentrations of B and P in the residual silicon liquid. However, HBO is a stable species in the vapor phase over a wide range of conditions, and is considered to be the most important species for removal of B to the vapor [28, 29].

## 8.4 SLAGGING

If an impurity can react to form a non-volatile species, it may be possible to incorporate the species or a combination of species to form a second phase, thereby sequestering the impurity away from MG silicon into this “slag” phase. Refining by slagging is dependent on several parameters, viz., reaction kinetics, diffusion of impurities, partition ratios, etc. Slag phase can either float on the surface of molten silicon or sink to the bottom of

the crucible and be removed. A synthetic slag can be added to the charge for refining or formed as a result of reactions with impurity elements. It is important that the components of the slag not contribute impurities to silicon which cannot be removed by later processing. MG silicon contains alkali and alkaline earth elements that are slag formers. The analysis carried out to review the impurity elements and evaluate their propensity to go into the slag phase show that the tendency is dependent on the acidity/basicity of the slag as well as the oxygen partial pressure. The results show that F, Al, P, S, Ca, Ga, Ge and Sr can be efficiently removed by slagging [30].

Liaw and D'Aragona [31] reported refining of MG-Si by slagging with CaO-SiO<sub>2</sub> and CaO-MgO-SiO<sub>2</sub>. The effectiveness of purification was evaluated by analyzing the impurity concentration in the ingots as well as in the slags. The results show that the slags consisting of CaO-SiO<sub>2</sub> and CaO-MgO-SiO<sub>2</sub> are effective for extracting aluminum from the MG-Si melts. The repeated melting and pulling method is effective for the removal of other metallic impurities.

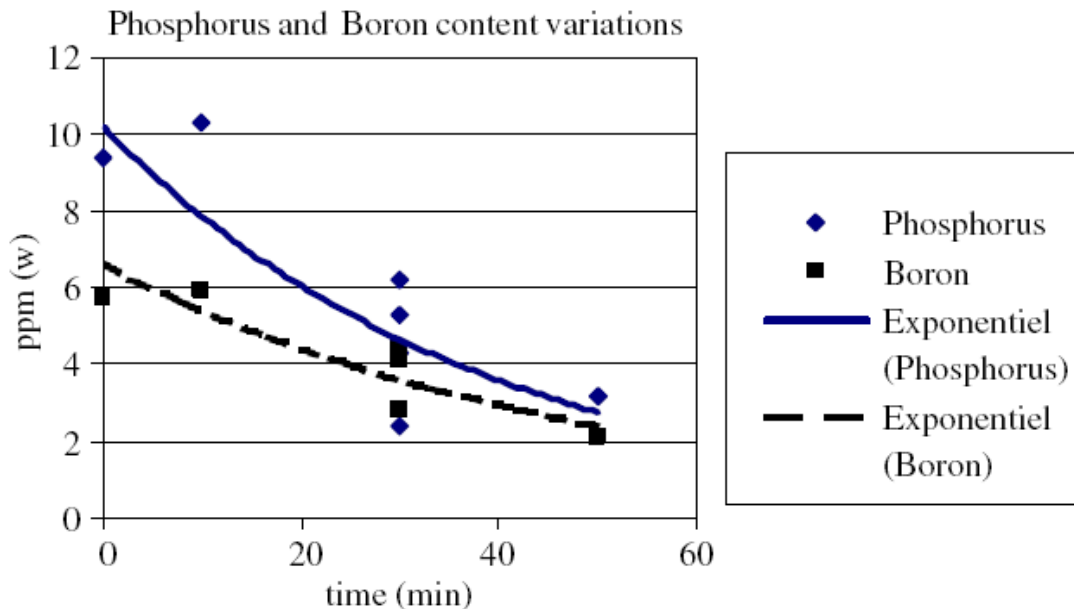
## **8.5 GAS BLOWING**

During refining of molten MG silicon, gases can be purged through the melt. These gases can react with the impurity elements, or be neutral to promote stirring of the melt. An advantage of a stirred melt is that it may limit the role of diffusion and promote reaction rates. Different gases have been used to promote rates as well as promoting conditions for slagging and oxidation. The gases have also been used to transport solids (slags), liquids (moisture) or gases (gas mixtures) to react with molten MG silicon and promote refining [28].

### **8.5.1 Boron and phosphorus removal by gas blowing**

Currently, large quantities of silicon scrap from the electronic industry are available that cannot be used for PV applications because of the very high B content. The B content of this silicon scrap is about 4 to 10 times that in MG silicon [29]. In order to remove the boron refining process involved moist gas blowing through molten silicon is employed. Boron can be extracted in the gaseous form as BOH, BO, BH<sub>2</sub> and B<sub>2</sub>O<sub>2</sub> but the vapor pressure of BOH is at least one order of magnitude larger than that of the other species in the temperature range 1500 – 1700°C [32]. Flamant *et al.* [33] conducted experiments at 0.05 atm to favor also P vaporization and with 1l/min Ar + 2.5ml H<sub>2</sub>O to favor B vaporization as BOH. Temperatures above 1500°C are needed in order to reach a significant P vapor pressure [33]. Phosphorus can form binary compounds with Si (Si<sub>2</sub>P, SiP) and phosphates such as Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>(OH),

which have a negligible influence on P vaporization [33]. Initial B and P contents were 5.7 and 9.4 ppm(m) respectively and after 50 min, the B and P contents in the sample were 2.1 and 3.2 ppm(m), respectively. Sample composition as a function of treatment time (10, 30 and 50 min) is illustrated in Figure 5.



**Figure 6:** Variation of boron and phosphorus contents as a function of treatment time. Pressure: 0.05 atm, argon: 1 l/min, water: 2.5 ml [33]

Khattak *et al.* [28, 29] reported better boron and phosphorus removal from molten silicon. Their results showed that using commercially available MG silicon B concentration can be reduced to about 0.3 ppma, well below the 1 ppma target for SoG silicon, and P to 7 ppma from original levels of 40-60 ppma. After the refining step, the melt was directionally solidified. It was shown that, except for B and P, other impurities were reduced to < 0.1 ppma. When silicon scrap is used, B levels were reduced to <1 ppma and refined material is used as feedstock.

## 8.6 SIMULTANEOUS REACTIONS

Theoretical analysis of the above refining processes indicates that different experimental conditions may be necessary for refining various impurity elements; for some elements, refining is not an isolated process. Experimentally, combination of the refining processes has shown even better results compared to the sum of the individual processes. This may be explained by the fact that vigorous stirring of the “melt”, “slag”, “impurities” and

“impurity species” are intimately mixed, thereby promoting reactivity and “tying up” the impurity, rather than its being restrained by diffusion. Similarly, impurities may be trapped in an oxidized state in the slag and removed thereafter by evaporation [29]. Simultaneous reactions may allow complex, local equilibrium steps to happen sequentially which would otherwise not happen.

## **9 INDUCTIVE THERMAL PLASMA FOR PURIFICATION OF METALLURGICAL GRADE SILICON**

Among many efforts to purify MG-Si in order to achieve solar grade silicon also the thermal plasma technique should be mentioned. Through this technique, MG-Si particles and powder are purified by partial evaporation and then being sprayed into liquid droplets on the surface of a ceramic substrate, creating thus a thin layer on this substrate in order to obtain photovoltaic properties [34].

Purification of the metallurgical powder is carried out in different steps. First, the silicon particles were injected into the plasma flow where they were heated, melted and their surfaces partially evaporated. This evaporation leads to the elimination of the surface impurities. The molten particles are then condensed onto a mullite substrate as liquid droplets. Finally, the liquid silicon is solidified through a horizontal displacement of the substrate under the plasma jet. Thus, the remaining impurities are concentrated in the last crystallized part according to the fusion zone principle. The last crystallized zone is finally eliminated by chemical treatment or by mechanical cutting. In this process, the efficiency of the in-flight fusion and purification depends on the temperature and chemical properties of the plasma regions crossed by the silicon particles, their residence time in the gas and their evaporation rate. Thus, in order to have the most effective purification, it is necessary to control all these parameters [35].

### **9.1 REMOVAL OF CARBON AND BORON FROM LIQUID SILICON BY THE USE OF A PLASMA ARC**

An attempt to remove carbon and boron from liquid silicon by a plasma arc combined with conductive heating is reported by Søliland [36]. The non-transferred arc was run with equal quantities of H<sub>2</sub> and Ar, containing 2 vol% and 4 vol% O<sub>2</sub> in the flow and with



temperatures of 1823 K and 1753 K. EG-Si was used with controlled amounts of C and B added before melting. Boron content in the liquid silicon was reduced from 35 ppmw to 20 ppmw during 100 minutes of oxidative plasma treatment. Due to contamination from the atmosphere above the liquid surface, the carbon level in the liquid silicon varies considerably. The reason for that might be the reaction between humidity contained in the furnace insulation and the graphite susceptor, producing CO gas.

## **10 SO-G SILICON FROM OPTICAL FIBERS WASTES WITH THERMAL PLASMAS**

Optical fibers, which are made of ultra-high pure silica glass containing a little germanium dioxide at the center called core, are key components of Information and Communication Technologies (ICTs). Production has increased with continued, rapid and sustained growth. The total optical fiber prepared by ultra-high-pure silica reached 29.8 million km corresponding to 810 ton of silica containing 370 ton of silicon in Japan in 2001. In addition, roughly similar amounts of pure silica was defective and wasted during the production process in the factory. According to the estimate, the trend for next 7 year aggregate growth is about 23%. Optical fibers used are a type of hazardous waste at present leading to waste of resources with ultra-high purity silica and high energetic potential without satisfactory treatment methods. Therefore, treatment and recycling of used and defective optical fibers is becoming more and more important.

Here the research done on recycling of optical fibers by thermal plasmas is mentioned. Material recycling processes using thermal plasmas are promising for hazardous wastes treatment, because thermal plasmas have unique advantages, such as high enthalpy to enhance the reaction kinetics, high chemical reactivity, oxidation and reduction atmosphere in accordance with required chemical reactions and rapid quenching to produce chemical non-equilibrium materials. A new way of silica optical fiber wastes recycling for feedstock supply of SoG-Si on the basis of harmless treatment with hydrogen-argon thermal plasmas is reported by Ma, Ogura, Kobayashi and Takahashi [37].

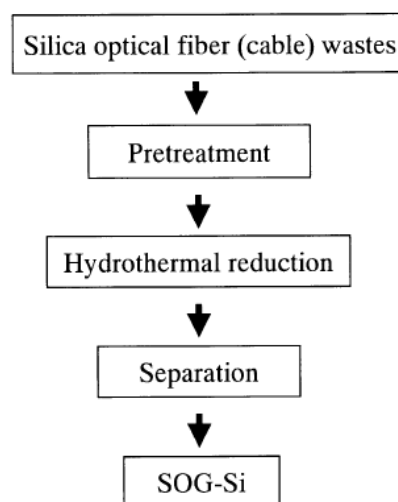
A plasma generator and a reactor with a continuous supply system of silica fiber pretreated reactant are employed in the process. The plasma generator, KOIKE plasma cutting system (Oxycut-80), was produced by Koike Sanso Kogyo Co., Ltd. The copper nozzle and

the quartz reactor with water-cooled were hand made. The typical operation conditions were the electric current at 50A and voltage at 25 V, and the gas flow rate of 200 and 1800 ml/min under atmospheric pressure for hydrogen and argon, respectively. The raw material for plasma reactions in optical fiber is pretreated at 900°C under air atmosphere for 2 h to remove the coating resin around the silica optical fiber and cut to 5mm in length.

Hydrogen plays important roles in the reduction of silica. Atomic hydrogen has high reactivity making it possible to decrease the content of impurities and intermediate products such as silicon carbide compared to carbon as reductant.

The results have shown that only diffraction peaks related to silicon were observed where one is attributed to SiO. This suggests that the property of silicon prepared by this method is not degraded even if a little germanium exists in the production. The content of metallic silicon for typical samples is 17 wt% and the average grain size is about 30 nm. Only the elements of silicon and oxygen in the production were detected [37].

A new simple production flow sheet proposed by authors for recycling of wastes with preparation of high purity silicon at low cost directly for feedstock supply of SoG-Si, is shown in Fig. 6. It suggests that silicon with high purity at low cost could be realized *via* a method separating metallic silicon and silicon oxides.



**Figure 6:** Sketch of the production flow sheet [37].

## 11 RECYCLING OF SLUDGE CONTAINING SILICON

More than 80% of the current solar cell production requires the cutting of large silicon crystals. While in the last few years the cost of solar cell processing and module fabrication could be reduced considerably, the sawing costs remain high.

The ingots are mainly cut by the multi-wire slicing technology [24]. Cutting is achieved by abrasive slurry, which is supplied through nozzles over the wire web and carried by the wire into the sawing channel. The slurry consists of a suspension of hard grinding particles. Today, SiC and diamond are the most commonly used abrasives. Both materials are very expensive and account for 25 to 35% of the total slicing cost. The volume fraction of solid SiC particles can vary between 20 and 60% and the mean grain size between 5 and 30  $\mu\text{m}$ . Kerf loss is of about 180  $\mu\text{m}$  when wafers between 200 and 300  $\mu\text{m}$  are cut. So, during wafer cutting, almost 50% of silicon is lost in the sludge [24].

Since large quantities of slurry and SiC are used during sawing much research is done on recycling sludge.

Kuniaki [38] developed a method to recycle the sludge by forming ceramics. In this method sludge is put into an iron pot and heated at 1140°C. In this step, Al, Na and Ca are removed while silicon remains as residual or an oxide. Then, the sludge is mixed with kaolin, containing quartzite, clay, feldspar, pottery stone etc., to a ratio of up to 60% kaolin. In the next step the mixture is calcined in a specific temperature and is ready to be used in pottery, building material (brick, roofing tile), paving stones etc.

Almost the same method for using the silicon sludge in the porcelain materials was developed by Yuji [39]. The recovered silicon slurry is added to the body containing ground and formulated porcelain or the starting material of ceramic wares containing a variety of components and additives, then, the mixture is formed, and fired to give ceramic wares. Thus, the silicon powder can usefully be utilized without soil pollution. Generally, since the water content of the silicon sludge is high, dehydration is employed to adjust the water content, if it is used as a starting substance for ceramic wares.

## SUMMARY

In the present paper, production, refining and recycling of silicon is described. Emphasis is on the refining and recycling of silicon for PV industry. The reason is the immense growth of photovoltaics every year where silicon is the dominant PV material with more than 98% of PV cells and modules based on it. This growth requires more and more silicon feedstock.

During the process of multi-crystalline production, more than two-thirds (68%) of the silicon feedstock that enters the PV production chain is lost during the different production steps in the form of different types of silicon containing waste. This quantity represents a potential silicon feedstock, especially since the quality of this silicon at the beginning was exactly matching the requirements of the PV production. In order to efficiently recycle silicon, the production and refining processes need to be clearly understood.

Attempts for a metallurgical route for the production of SoG silicon feedstock is reported. This can be achieved within the metallurgic silicon industry by applying pre-purification techniques to the low-quality metallurgical grade (MG) silicon. In order to arrive at SoG silicon, newly developed plasma purification processes together with other purification processes, like slagging, acid leaching, alloying process, directional solidification, and gas blowing are addressed. These techniques will use this SoG silicon as starting material for standard multi-crystalline PV production. Further development work towards the refining methods is necessary.

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