CHAPTER 12.33

Silica, Quartz, and Silicon

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SILICA AND QUARTZ

Silica, also known as quartz (SiO_2), is categorized by statistical historians as sand and gravel. It is divided into two categories of commodities: construction-grade and industrial-grade sand and gravel.

Industrial-grade sand and gravel generally has silica content that is much higher than that of construction grade in some instances, such as in glass production where the silica content will be as high as 99.9% SiO_2. Production levels of silica are relatively unchecked on a world basis; however, U.S. production of the two grades in 2014 was 911,000 t (metric tons) and 75,000,000 t of construction-grade and industrial-grade silica, respectively. Industrial-grade silica is used in the production of glass (39% of the total), foundry sand (22%), and abrasives (5%), and the remaining 34% is used in a multitude of products, which include fracking sand in the production of petroleum and lump ore used in the production of ferrosilicon and metallurgical-grade silicon (MG-Si).

Construction-grade sand and gravel is even less specific in that 50% of the products are unspecified while the second half is generally categorized as being concrete for road construction, additives for asphalt, and the remaining used in concrete blocks, bricks, pipe, and roofing shingles.

COMMERCIAL USES OF SILICON METAL

Silicon is a metalloid, and its primary use over the past century has been as an alloying agent. Thus, it has typically been referred to as a metal. Silicon as an element begins to take on metallic properties at temperatures above 1,000 K (727°C). Silicon metal (Si) is produced most commonly in an electric arc furnace, reducing SiO_2 to Si metal (covered in detail in the "Production of Metallurgical-Grade Silicon" section later in this chapter). The products from this industry are dependent on the demand for the various end uses, typically silicon ferroalloy and silicon metal. Silicon ferroalloy, or ferrosilicon, is produced for alloying in cast iron, cast steel, and steel. Silicon metal, or MG-Si, is used to alloy with aluminum and in the production of chemicals, particularly silicones, and, to a lesser degree, in the production of high-purity silicon for the photovoltaic industry (i.e., solar-grade silicon), and in the production of ultra-high-purity silicon in the semiconductor industry (i.e., electronic-grade silicon).

Silicones Production

Silicones, or organosilicon compounds, are produced throughout the world using direct synthesis, the Rochow process, and/or the Müller–Rochow process, typically as a common technology on an industrial scale. The process can be completed using alkyl halides in a copper-catalyzed reaction with silicon metal. Processing is conducted in a fluidized bed reactor. The best result in terms of both selectivity and yield occurs with use of methyl chloride. Typical conditions for the production to occur are at temperatures of 573 K (300°C) at 2–5 bars of pressure. These conditions allow for 90%–98% conversion for silicon and 30%–90% for chloromethane. Approximately 1.4 million t of dimethyldichlorosilane (Me_2SiCl_2, where Me represents CH_3) is produced annually using this process (Elschenbroich 1992). The generalized chemical reaction for the production of organosilicon compounds is as follows:

$$\text{xMeCl} + \text{Si} \rightarrow \text{H}_2\text{MeSiCl, Me}_2\text{SiCl}_2\text{, MeSiCl}_3\text{, and many other products} \quad \textbf{(EQ 1)}$$

Ultra-high-purity silicon metal for use in electronics and high-purity silicon metal for use in photovoltaics are presented in detail in the "Metallurgical-Grade Silicon Applications" section later in this chapter. Each of these products are produced using chlorine-based chemistry and are completed utilizing hydrogenation and distillation of trichlorosilane to produce the base chemicals, which are further refined through thermal decomposition to produce polycrystalline silicon (poly-Si) of very high purity. Further treatment of the poly-Si is required to produce the electronic-grade single-crystal silicon during this refining process. Poly-Si is produced in rod or granular form depending on the technology employed. Poly-Si rods, having diameters of 60–300 mm, are produced in Siemens reactors. Poly-Si is sold in rod form or the rods are broken into smaller particles (i.e., minus 10 cm and sold in a chunk form). Typically, chuck is sold in 5-kg bags. Granular

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silicon, generally the size of rock salt and 5–10 mm in diameter, is produced using fluid bed reactors. Granular poly is sold in bags from 5 kg up to 1,500-kg super sacks.

SOURCES OF QUARTZ AND SILICA FOR PRODUCTION OF SILICON

Quartz is the second most common mineral in the earth's crust. It is found in all three of the earth's rock types: igneous, metamorphic, and sedimentary. Quartz is colorless but is frequently colored by impurities, such as iron, and may then be almost any color. It may be transparent to translucent, hence its use in glassmaking, and has a vitreous luster. Quartz is a hard mineral, rating 7 out of 10 on the Mohs scale of mineral hardness, owing to the strength of the bonds between the atoms. It will scratch glass. It is also relatively chemically inert and does not react with dilute acids. These are desirable qualities in various industrial uses. Figure 1 shows Brazilian quartz crystals.

Quartz is particularly prevalent in sedimentary rocks since it is extremely resistant to chemical breakdown via the weathering process. Physical weathering—such as erosion as a result of freeze and thaw, rain splash, and surface runoff resulting in abrasion—produces silica sands and sandstones that are of great use to the industry in many areas, such as construction, landscaping, and fiberglass production. However, most of the quartz/silica that is used by the industry for the production of silicon metal is the metamorphic form of quartz or the mineral quartzite (Schei et al. 1998). Sandstone is converted into quartzite through heating and pressure usually related to tectonic compression within orogenic belts. When sandstone is cemented to quartzite, the individual quartz grains recrystallize along with the former cementing material to form an interlocking mosaic of quartz crystals. Most or all of the original texture and sedimentary structures of the sandstone are erased by the metamorphism. The grainy, sandpaper-like surface becomes glassy in appearance. Minor amounts of former cementing materials, iron oxide, silica, carbonate, and clay often migrate during recrystallization and metamorphosis. This causes streaks and lenses to form within the quartzite.

Pure quartzite is usually white to gray, though quartzite often occurs in various shades of red because of varying amounts of iron oxides (FeO, Fe_2O_3, and Fe_3O_4). Other colors of quartzite include yellow, green, blue, and orange, which occurs because of other chemical or mineral impurities. High-grade silica is found in unconsolidated deposits below thin layers of overburden or in metamorphic deposits that sometimes are millions of metric tons (i.e., deposits that result in mountains).

For industrial use, high-purity deposits of silica capable of yielding products of at least 95% SiO_2 are required. Often, even higher purity values are needed. Silica is produced by strip mining, quarrying methods, and open pit mining; it is rare that extraction is by underground mining methods. Additionally, very little or no physical processing is normally required to produce high-grade silica products, due to the high-grade deposits that are currently found in the world. Often, the only processing is by human interaction in the course of sorting, visual observation, and physical removal of undesired rock types and other waste products (i.e., wood or other organic matter).

The preferred quartzite deposits, which are used by smelters in the reduction of silica to silicon metal, are those that produce "lump" silica. The size is variable but normally consists of 80% in the range of 75 to 150 mm lump, with the other 20% being smaller in size. The lump quartzite retards compression in the shaft of the electric arc furnace because of the toughness of the mineral, providing the needed voids in the furnace charge and allowing the hot gases of the furnace to easily move upward through the burden. More on the dynamics of the electric arc furnace is covered later in this chapter.

Figure 1 Brazilian quartz crystals

Depending on how the silica deposit was formed, quartz grains may be sharp and angular, subangular, subrounded, or rounded. Foundry and filtration applications require subrounded or rounded grains for best performance.

Historical pricing of silicon metal products is shown in the following list for the period of 1995 through 2014. The pricing of these products has fluctuated significantly with pricing in the five-year period from 2000 through 2005 having some lower pricing than that which occurred during the previous five-year period (i.e., 1995 through 1999). The source of pricing information is the U.S. Geological Survey's *Minerals Yearbook* (USGS 1996–2015).

- Ferrosilicon (50% Si): \$0.41–\$1.16 per lb
- Ferrosilicon (75% Si): \$0.32–\$1.09 per lb
- Metallurgical Si (>96.5% Si): \$0.51–\$1.62 per lb

Both the construction industry and other commodity pricing are variable and the number of commodities that exist does not allow for listing. Resources for pricing should be checked by the investigator at the time of need.

MINERAL PROCESSING OF SILICA AND QUARTZ

Impurities in quartz play a significant role in ore selection and the degree of mineral processing required for its use in production of silicon, optics, optical fiber, glass, plastics, and high-temperature refractories. The shape, size, surface texture (rounded versus sharp edges), and crystal structure of granular quartz has a significant effect on product choices for foundry and fracking sands, concrete, bricks, sand traps (golf), sandboxes, and playgrounds.

Mine-site selection and the degree of mineral processing of quartz is dictated by product specifications, ore mineralogy, and production method. An example of the latter is the production of silicon in the silicon-submerged arc furnace where quartz lumps from mines, or river rocks, are charged to the

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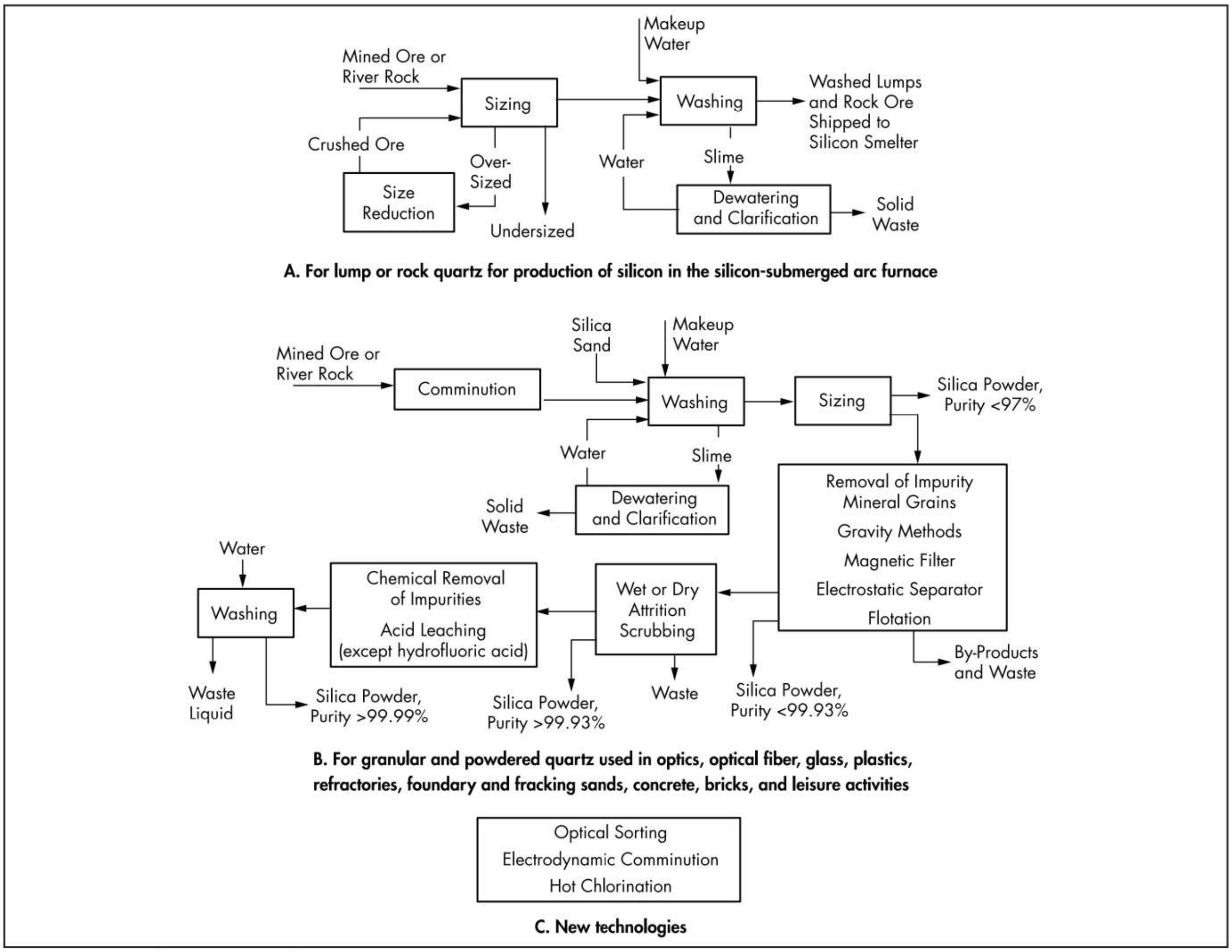

Figure 2 Mineral processing of quartz

furnace. The control of impurity content rests largely with ore selection, as impurities remain locked in the lumps and rocks, and thus mineral processing amounts to only sizing and washing of the ore, as shown in Figure 2A.

Meeting product specifications with granular and powdered quartz often requires greater mineral processing, as presented in Figure 2B. Comminuted ore consists of five classes of impurities:

1. Separate grains of other minerals, either present in quartz sand or liberated upon crushing and grinding of lump ore
2. Impurity minerals attached to quartz grains, or impurity atoms that have diffused into the quartz but are concentrated in a thin skin at the surface
3. Impurity minerals that extend from the surface and into the grain itself
4. Impurity minerals contained within the grain of quartz
5. Impurity atoms that substitute for either Si or O atoms throughout the grains

Comminuted ore provides more opportunities for removal of impurities than lump and rock ore used to produce silicon, as indicated in Figure 2B. The purities indicated in the figure are approximate numbers; purity <97% is used for playgrounds, sandboxes, sand traps; purity <99.93% is for foundries, fracking, glass, and bricks; purity >99.93% is for specialty glass, high-temperature refractories, and plastics; purity >99.99% is for optics and optical fiber. Individual grains of other minerals can be removed after washing and sizing by any or all of several methods: electrostatic separator, flotation, magnetic filter, and gravity methods. The latter includes jigs, shaker tables, spirals, and so forth. Attrition scrubbers produce a high-shear environment in which particles scrub against themselves to scour their surface, removing both contaminated surface silica and deleterious minerals bonded or physically attached to the surface of the quartz grains. If impurity minerals extend from the surface into the body of the grain, acid leaching can be used in their removal. Impurity minerals are immune to acid leaching if they are encapsulated by silica. Thus, the success of acid leaching is dependent on the degree of comminution. Unfortunately, impurity atoms (Al, B, P, and S) that substitute for either Si or O in the quartz remain with the quartz.

Newer mineral processing techniques identified in Figure 2C are all being employed by Anzaplan GmbH. The coupling of optical images and high-speed computer to operation of mechanical devices makes optical sorting on the basis of color, transparency, and shape a means for improved quality

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control of quartz products for the glass, optics, foundry, and cement industries. Electrodynamic comminution uses electrical-induced shock waves that fracture minerals along their weaker natural boundaries. Those boundaries exist between different minerals in composite rock. In processing of quartz, electrodynamic comminution exposes impurity minerals, making their removal by acid leaching possible. Hot chlorination can replace the use of acid. This technique relies on the volatility of metal chlorides. Passing granular or powdered quartz through a hot gas (~1,300 K [1,027°C]) containing chlorine or hydrogen chloride will remove most metallic minerals from quartz, provided the impurities are not isolated from the gas.

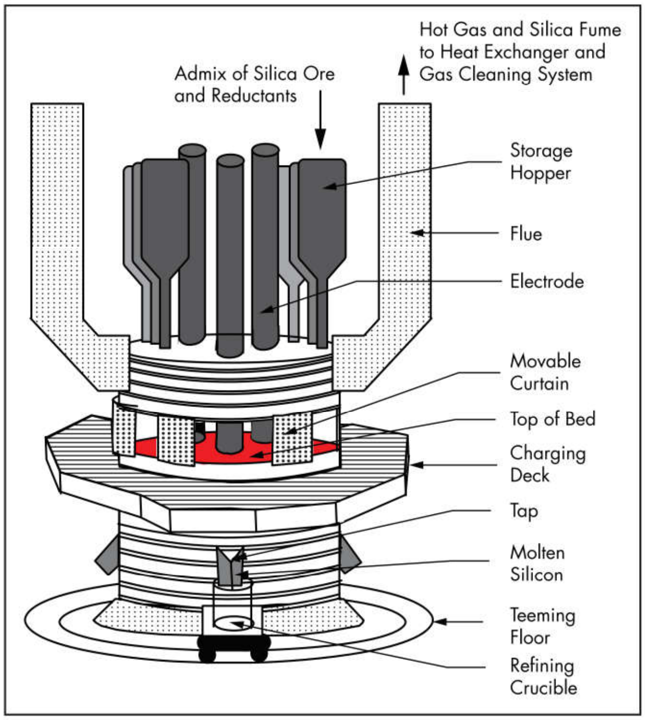


Figure 3 Silicon-submerged arc furnace

The degree of mineral processing of quartz is dictated by product specifications and production cost; those factors are linked by ore selection and its mineralogy. Successful development of a quartz deposit requires careful evaluation of all these factors.

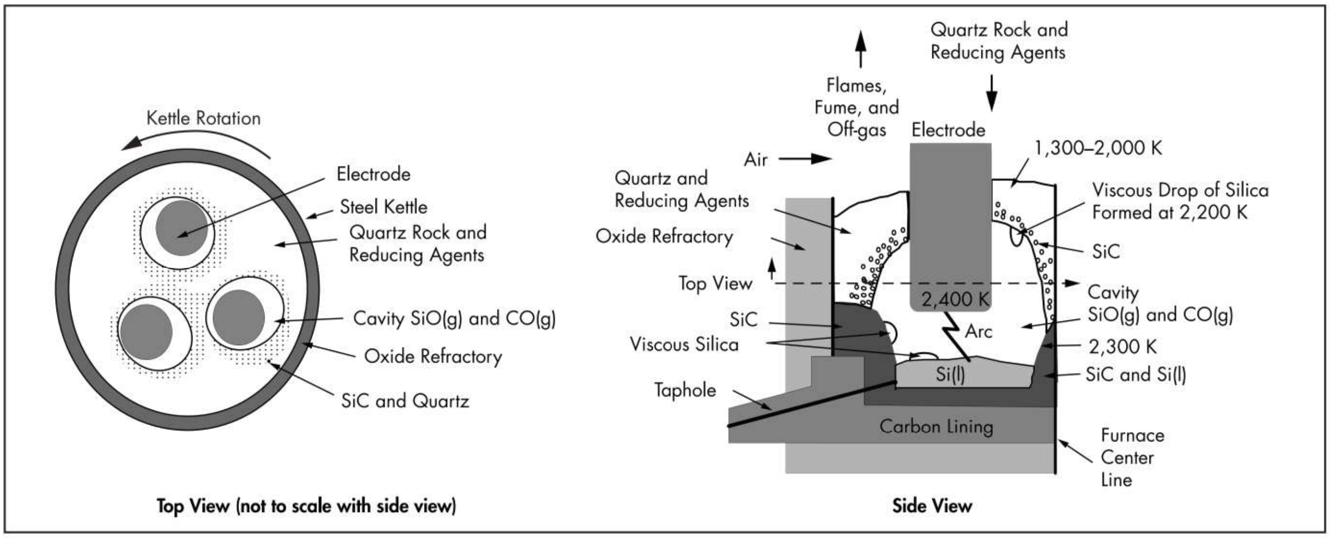
PRODUCTION OF METALLURGICAL-GRADE SILICON

Silicon-Submerged Arc Furnace

Metallurgical-grade silicon (MG-Si) and ferrosilicon are produced in the silicon-submerged arc furnace, where ore and reductants are processed at temperatures as high as 2,400 K (2,127°C). The arc furnace, as shown in Figure 3, is the centerpiece to a modern silicon plant. The raw materials (silica ore, coke or coal, and wood chips) are delivered to the plant and stored in covered sheds. Operators, using sophisticated computer programs and automated controls, draw on the stored materials, mix them, and transport the furnace feed to hoppers above the arc furnace. When needed, the operator releases the furnace feed so that it falls onto the bed material in the furnace. Movable curtains allow workers on the charging deck easy access to the furnace to use mechanized rakes to smooth out the piles of new furnace feed, maintaining bed height and filling in blowholes formed since the previous addition of furnace feed.

Countercurrent flow exists in the furnace; gases generated in the hottest portion of the furnace pass up through the bed of solids that move downward. The latter is consumed in the production of silicon and in generation of gases. Silicon is extracted from the furnace through tap holes and allowed to collect in the refining crucible. Gases emanating from the top surface of the bed are drawn off, along with air, to the heat exchanger and gas cleaning system. Silica fume is collected from the gas cleaning system. The furnace can be operated to produce commercial quantities of both silicon and silica fume.

The hearth of the furnace is rotated around the fixed electrodes, resulting in a cavity forming around each electrode, as shown in Figure 4. The cavity serves to promote radiant heat transfer to satisfy energy requirements for the endothermic



Adapted from Schei et al. 1998

Figure 4 Interior of the silicon-submerged arc furnace

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reactions occurring in and around the cavity. Newly charged material caves in behind the electrode as the kettle is rotated, renewing the porosity of the bed, while on the other side of the electrode, older furnace feed with less porosity is consumed. The drawing also shows that SiC builds up around the hearth, protecting it from thermal and physiochemical corrosion. Furnace linings typically last two years, and the lining in a well-run furnace will last three years.

Chemistry in the Arc Furnace

The overall reactions in producing silicon are

$$SiO_2 + 2C \rightarrow Si(l) + 2CO(g) \qquad \textbf{(EQ 2)}$$

(composite reaction occurring within the bed)

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \textbf{(EQ 3)}$$

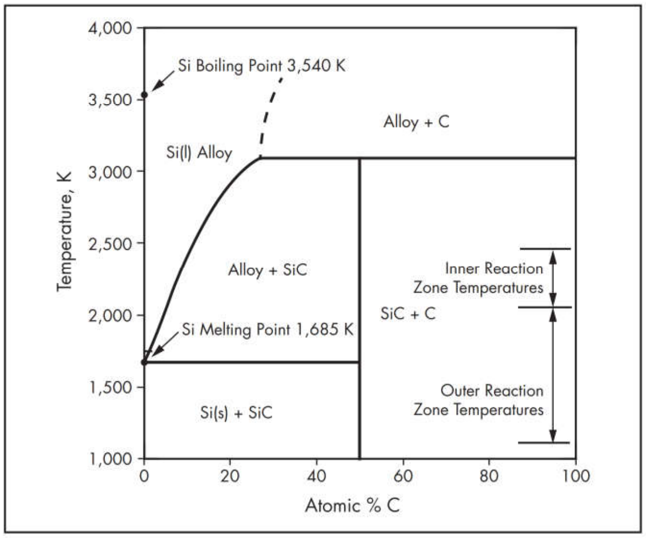
(occurs as off-gas exits bed)

$$2SiO(g) + O_2(g) \rightarrow 2SiO_2 \qquad \textbf{(EQ 4)}$$

(silica fume produced as off-gas exits bed)

The composite Reaction 2 is composed of several reactions occurring in the furnace. While there have been many studies of the silicon-submerged arc furnace (reviewed in Schei et al. 1998), it was Anders Schei in 1967 who published the classical equilibrium diagram used, along with the Si-C phase diagram, to explain reactions occurring in the arc furnace. Through use of the equilibrium diagram and the Si-C phase diagram, the bed within the furnace is viewed as consisting of inner and outer reaction zones. The demarcation between zones is the transformation of all carbon in the reductants to SiC, which in well-run furnaces occurs at a temperature of approximately 2,050 K (1,777°C). The phase diagram in Figure 5 reveals that silicon cannot coexist in equilibrium with carbon at temperatures below 3,100 K (2,827°C), thus the necessity that all carbon be converted to SiC.

Schei's equilibrium diagram (with modifications in Lynch 2002) is presented in Figure 6. Using the phase rule, Schei (1967) demonstrated that any equilibrium condition within the arc furnace can only involve two condensed phases. The equilibrium diagram, which is presented in two graphs, represents all possible equilibrium reactions. Figure 6A represents conditions in the upper bed (outer reaction zone) where it is essential to reduce the SiO content in the gas to ensure significant Si yield for the overall process. Figure 6B reflects the conditions in the inner reaction zone where molten Si is produced. The diagram reflects the high temperatures and significant partial pressure of SiO(g) necessary to produce Si.



Adapted from Schei et al. 1998

Figure 5 Si-C phase diagram

Analysis of reactions occurring in the arc furnace begins with the outer reaction zone and with knowledge that the gas in the inner reaction zone has significant concentration of both CO and SiO, while the gas leaving the furnace is primarily CO. Quartz ore, coal (or coke), and wood chips are dropped from the storage hopper onto the bed in the furnace, where the temperature is 1,300 K (1,027°C) and higher. The heat and the reducing nature of the gas exiting the bed convert the wood chips to charcoal. That charcoal, while a source of impurity elements, is essential to maintaining a porous bed through which gases can flow from the inner reaction zone and through the bed material in the outer zone. The SiO content in the gas as it moves through the outer zone declines owing to any of the following reactions:

$$SiO(g) + 2C \rightarrow SiC + CO(g),\ \Delta H_{1473K} = -78.3\ \text{kJ},\ T \geq 1{,}473\ \text{K} \qquad \textbf{(EQ 5)}$$

$$2SiO(g) \rightarrow SiO_2 + Si,\ \Delta H_{1273K} = -688.9\ \text{kJ},\ T \geq 1{,}273\ \text{K} \qquad \textbf{(EQ 6)}$$

$$3SiO(g) + CO(g) \rightarrow SiC + 2SiO_2,\ \Delta H_{1785K} = -1{,}415.7\ \text{kJ},\ T \geq 1{,}785\ \text{K} \qquad \textbf{(EQ 7)}$$

$$SiO(g) + CO(g) \rightarrow C + SiO_2,\ \Delta H_{1785K} = -668.5\ \text{kJ},\ T \leq 1{,}785\ \text{K} \qquad \textbf{(EQ 8)}$$

The equilibrium conditions for these reactions are presented in Figure 6A, some written in the reverse direction. The enthalpy of these reactions reveals that consumption of SiO(g) moves heat from the cavity into the upper bed. That evidence—light brown deposits or white deposits with brown spots—from excavation of cooled furnaces reveals that Reaction 6 is the most important reaction in moving heat into the upper bed (Schei et al. 1998). Kinetic issues play important roles in determining which reactions occur at meaningful rates. The temperature listed with each reaction represents conditions where they occur. Reaction 8 is not thought to be significant much below the temperature indicated.

The movement of heat to the upper bed plays an important role in converting carbon to SiC. The equilibrium line for Reaction 6 lies in the unstable gas region (defined by the line connecting points i, b, and g in Figure 6A, and with the line connecting points g, h, and i in Figure 6B, indicating that the rate of Reactions 7 and 8 are slow in comparison and that a pseudo equilibrium is established by Reaction 6. At temperatures below 1,473 K (1,200°C), Reaction 6 dominates and SiO(g) decomposes, depositing SiO_2 and Si on the ore and reductants, and raising their temperature. At 1,473 K (1,200°C), SiO(g) concentration is not so depleted by Reaction 6 as to prevent reaction between the gas and C to produce SiC as per Reaction 5. At temperatures higher than that at point b in Figure 6A, Reaction 5 continues to reduce the SiO(g) content in the gas passing up and out of the inner reaction zone. Production of SiC continues until all the carbon is consumed. The equilibrium line for Reaction 5 in Figure 6A extends into Figure 6B, which is not shown in the latter figure

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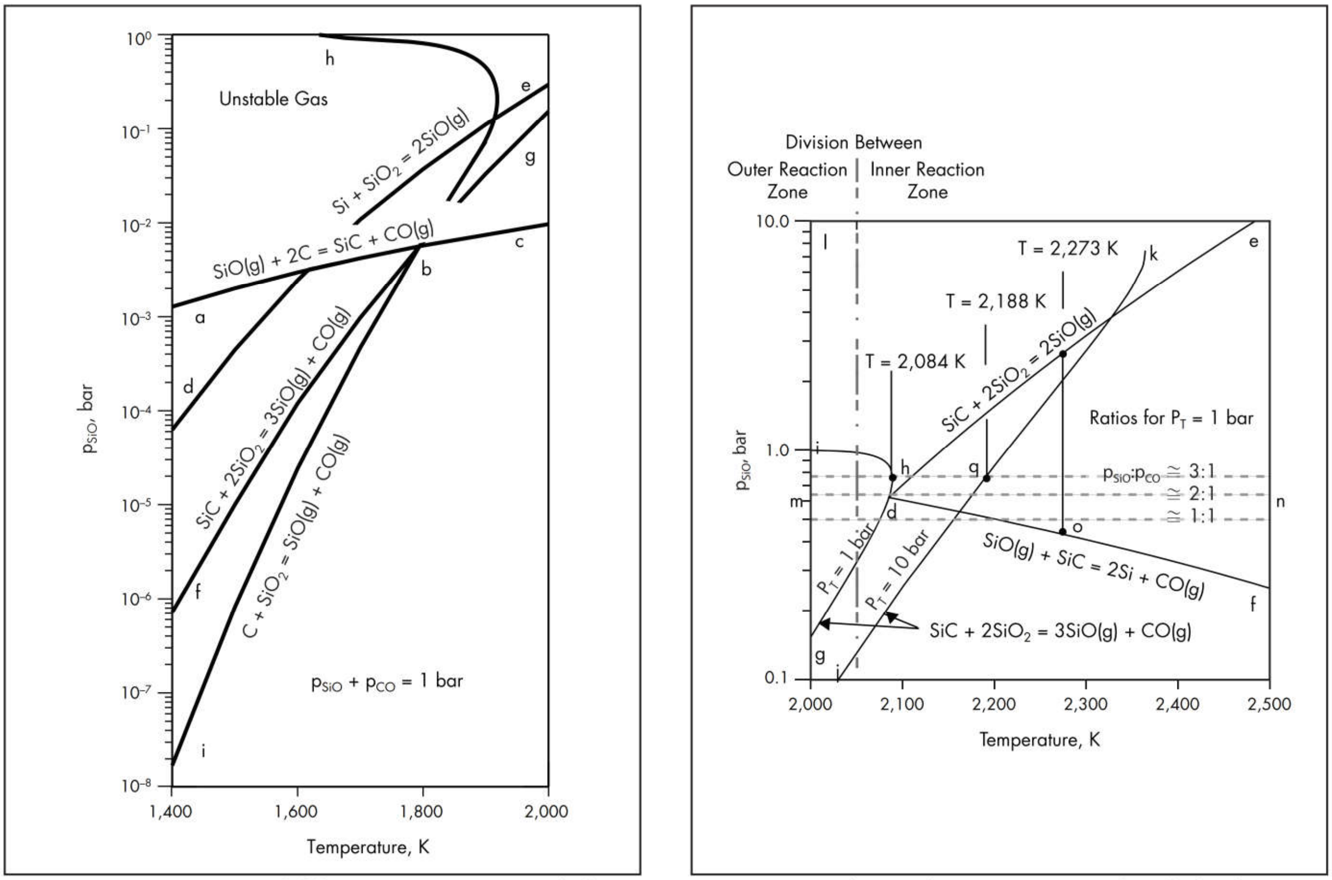

A. Lower temperatures are typical of the outer reaction zone (upper bed)

B. Represents conditions in the inner reaction zone (lower bed and cavity)

Adapted from Schei et al. 1998

Figure 6 Stability diagrams for reactions occurring in the silicon-submerged arc furnace

because the equilibrium vapor pressure associated with the reaction is lower than that plotted.

The production of Si requires that all carbon entering the inner reduction zone be converted to SiC. While Si and C cannot coexist in the arc furnace, Si and SiC can, as shown in the Si-C phase diagram (Figure 5). Too much C charged to the furnace will cause SiC to build up in the bottom of the hearth. That buildup will push the electrodes up and out of the furnace. Charging too little C will cause the Si yield to drop as silica fume is formed when SiO(g) leaves the furnace.

There is a balance between SiC entering the inner reaction zone as well as its consumption in the production of Si. Reactions occurring in this zone are represented by the equilibrium lines presented in Figure 6B. Silicon is produced by the following reaction:

$$\mathrm{SiO(g) + SiC \rightarrow 2Si(l) + CO(g)},\ \Delta H_{2084K} = 166.6\ \mathrm{kJ},\ T \geq 2{,}084\ \mathrm{K} \quad \textbf{(EQ 9)}$$

That reaction requires SiO(g) that is produced by both

$$\mathrm{SiO_2(l) + Si \rightarrow 2SiO(g)},\ \Delta H_{2084K} = 606.1\ \mathrm{kJ},\ T \geq 2{,}084\ \mathrm{K} \quad \textbf{(EQ 10)}$$

and

$$\mathrm{SiC + 2SiO_2(l) \rightarrow 3SiO(g) + CO(g)},\ \Delta H_{2084K} = 1378.7\ \mathrm{kJ},\ T \geq 2{,}084\ \mathrm{K} \quad \textbf{(EQ 11)}$$

All three reactions are endothermic, particularly Reactions 10 and 11.

Production of SiO(g) is necessary for producing silicon. In Figure 4, viscous drops of SiO_2 fall into the pool of molten silicon at a temperature approaching 2,300 K (2,027°C). Examination of Figure 6B reveals that the equilibrium vapor pressure of SiO(g) at 2,300 K (2,027°C) for Reaction 10 is about 2 bars. Since the total pressure in the arc furnace is 1 bar, Reaction 10 can never achieve equilibrium. There is a similar situation for Reaction 11. Equilibrium conditions for that reaction are plotted for total pressures of 1 and 10 bars. The location of those two equilibrium lines indicates that any contact of SiC and SiO_2 at temperatures above 2,084 K (1,811°C) can only achieve equilibrium at total pressures >1 bar. At 2,300 K (2,027°C), the equilibrium vapor pressure is well above 10 bars. In the inner reaction zone at the higher temperatures, SiO(g) production by Reactions 10 and 11 cannot be stopped. The SiO(g) is either consumed in the production of Si by Reaction 9, or the gas passes up through the bed where most of it reacts with C in production of SiC, or it condenses as per Reaction 6.

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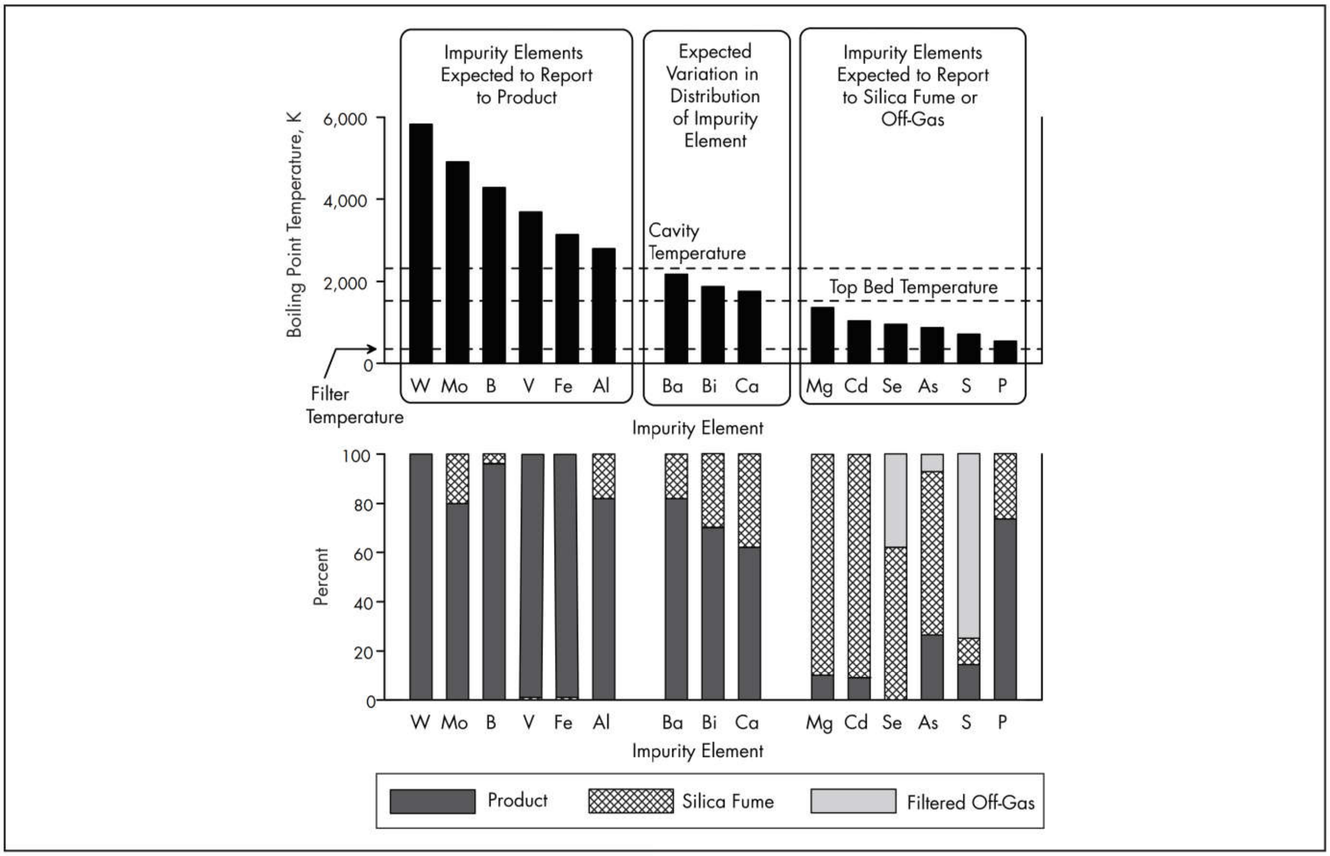
Kinetic factors play important roles in the composition of the gas leaving the inner reaction zone. Widespread condensation of SiO(g) by Reaction 6 on reductant and SiC ensure good contact between SiC and the SiO_2 required for Reaction 11. The energy requirement is substantial, and the source of that energy is likely photon transfer and convective heat transfer in the cavity. Similarly, the intimate contact between SiO_2 and Si produced by Reaction 6 is reversed as the material enters the cavity; again, heat transfer is the same as for Reaction 11. Reaction 10, as noted previously, also occurs when viscous drops of SiO_2 fall into the pool of molten Si, which acts as a source of energy. Silicon above 1,000 K (727°C) takes on metallic characteristics; thus the molten Si in the arc furnace is a good conductor of thermal energy, which is further enhanced by the turbulent conditions created by the arc striking the pool of Si. The area of contact between the drops and Si is limited compared to the contact created when SiO(g) is precipitated as silica and Si in the outer reaction zone. Reactions 10 and 11 feed SiO(g) for production of Si by Reaction 9. Consumption of SiO(g) by the reaction is considered to be faster than the rate of its production. Thus, gas composition in the cavity around the electrodes is established by Reaction 9. The equilibrium line for the reaction has negative slope in Figure 6B, and, thus, higher temperatures in the cavity are preferred to reduce the concentration of SiO(g) rising through the bed.

Impurities

Si refining is dependent on its final use; minimum refining for the steel and aluminum industries and maximum refining for the electronics industry are covered in the next section. A significant fraction of impurities entering the arc furnace in the ore as well as reductants are retained in the Si leaving the furnace. Myrhaug and Tveit (2000) performed an extensive mass balance on the retention of impurities in ferrosilicon leaving the silicon-submerged arc furnace, coming up with the boiling-point model. Some of their results are presented in Figure 7, where elements with boiling-point temperature higher than the cavity temperature are expected to dissolve in the Si product. Elements with boiling-point temperatures below that of the top bed material should leave the furnace with either the silica fume or the off-gas. The one anomaly is phosphorus, which should be volatilized but primarily enters the final product. Unfortunately, P as well as B are the two most difficult elements to remove from Si and require critical control in Si used by both the electronic and photovoltaic industries.

With large arc furnaces, tapping is continuous. SiO_2-rich flux can be added to the MG-Si flowing into a refining crucible to create a slag. The silica in the flux is reduced by Al and Ca dissolved in the Si, producing a slag consisting primarily of SiO_2, Al_2O_3, and CaO. Depending on the combined Al_2O_3 and CaO content of the slag, it either floats on top of the molten



Adapted from Myrhaug and Tveit 2000

Figure 7 Myrhaug and Tveit's boiling-point model and test results

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Table 1 Annual production for silicon, in thousands of metric tons

Product	Circa 1997	2008	2009	2014
Silicon metal	980	1,680* + 210†	1,800* + 160†	2,600* + 200†
Ferrosilicon	2,600	~4,270	~4,350	~5,310
Total silicon	3,580	6,160	6,310	8,110

Data from Schei et al. 1998; USGS Mineral Commodity Summaries 2010, 2011, 2016; USGS Minerals Yearbook 2011, 2014

*Does not include U.S. production.

†Authors' estimate of U.S. production.

Si or sinks. Droplets of slag passing through the molten Si improve the refining action and also trap SiC particles that are likewise slowly sinking through the silicon. After sufficient refining time, the Si is cast in shallow trays.

METALLURGICAL-GRADE SILICON APPLICATIONS

The world production figures for silicon metal, and silicon in ferrosilicon, are presented in Table 1. In 2014, total domestic consumption from all sources, domestic and foreign, of silicon metal of purity <99.6% was 187,000 t, of which 15% was used primarily in producing aluminum alloys and the remainder used to produce silicones and other chemicals. Similarly that same year, 164,000 t of ferrosilicon was used in steel production and 23,000 t used in producing cast iron (USGS *Minerals Yearbook* 2014).

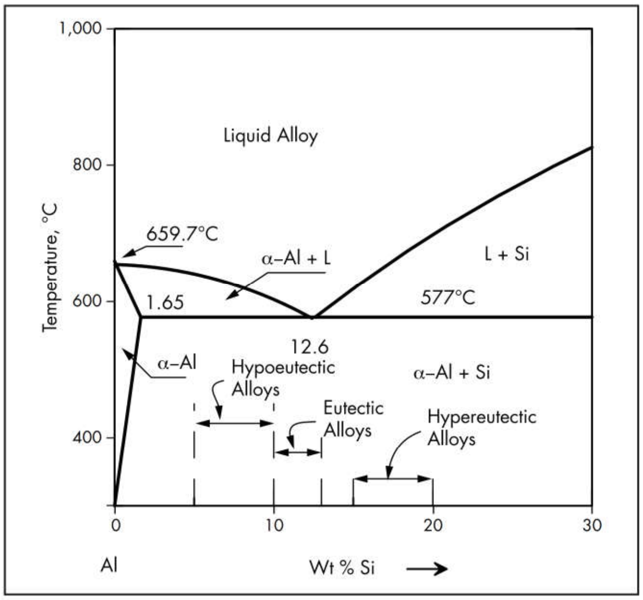
Worldwide production of high-purity silicon for electronics and photovoltaics amounted to 74,000 t in 2009. In 2010 to 2014, it is estimated that less than 5% of all silicon metal production was used in this capacity (USGS *Minerals Yearbook*, 2009–2014). While the percentage mass of silicon metal used in electronics and photovoltaics is small in comparison to other uses, its value on a per-mass basis far exceeds that of silicon used in other applications. Thus, much of this section is devoted to the purification of silicon.

Aluminum

Adding silicon to aluminum or aluminum alloys results in a strong, light alloy. As a result, these alloys are increasingly used in the automotive industry to replace heavier cast-iron components. This allows weight reductions, a reduction in fuel consumption, increased efficiencies, and reducing gas emissions. The Al-Si binary phase diagram shows that a eutectic point exists at 850 K (577°C) and 12.6% silicon (Figure 8). At this temperature and Al-Si composition, the melting point is lower than the melting point for pure silicon or pure aluminum (ASM International 1992).

There are three classes of aluminum foundry alloys that are based on their silicon content (Sigworth 2014):

1. **Hypoeutectic alloys.** These alloys have a silicon content less than the eutectic composition. Most of the common hypoeutectic alloys have between 5% and 10% silicon. Some examples: C355, 356, 357, and 359. These alloys are designed primarily for high-strength applications where good ductility is also required.
2. **Eutectic alloys.** These alloys have between 10% and 13% silicon and consist mainly of Al-Si eutectic in the cast structure. They have a narrow freezing range, excellent fluidity, and are easy to cast. They also have good wear resistance and are quite ductile when not alloyed and heat treated to high strength. Eutectic alloys containing Cu, Mg, and sometimes Ni are used extensively for pistons.



Adapted from ASM International 1992

Figure 8 Al-Si phase diagram

3. **Hypereutectic alloys.** These alloys have between 15% and 20% silicon, so their cast structure is composed of primary silicon particles embedded in a matrix of Al-Si eutectic. These materials have remarkable wear resistance and are used where this characteristic is desired: for pistons, liner-less engine blocks, and compressor parts. They also have good high-temperature strength but are difficult to machine. Diamond tools are necessary.

Silicone

Methyl Chloride Production

Methyl chloride is produced by condensing methanol with hydrochloric acid:

$$\underset{\text{methanol}}{CH_3OH} + \underset{\text{hydrochloric acid}}{HCl} \rightarrow \underset{\text{methyl chloride}}{CH_3Cl} + \underset{\text{water}}{H_2O} \qquad \textbf{(EQ 12)}$$

Two methyl groups (CH_3) must attach to each silicon atom to produce one molecule of dimethyldichlorosilane, which is the basic silicone building block. Methanol is a major ingredient in the manufacturing of silicone.

Chlorosilanes Synthesis

Chlorosilanes are synthesized in a fluid bed reactor at temperatures ranging from 523 K to 573 K (250°C to 300°C) and at pressures of 1–5 bars. The methyl chloride (CH_3Cl) flows through a fluidized bed of silicon metal powder. The reaction, which is catalyzed by a copper-based catalyst, generates a complex mix of methyl chlorosilanes:

$$x\text{Si} + y\text{CH}_3\text{Cl} \rightarrow \text{methyl chlorosilanes} \qquad \textbf{(EQ 13)}$$

The methyl chlorosilane mix contains (Me = CH_3)

- A large amount of dimethyldichlorosilane (Me_2SiCl_2)—the primary building block,
- A moderate amount of methyltrichlorosilane ($MeSiCl_3$),

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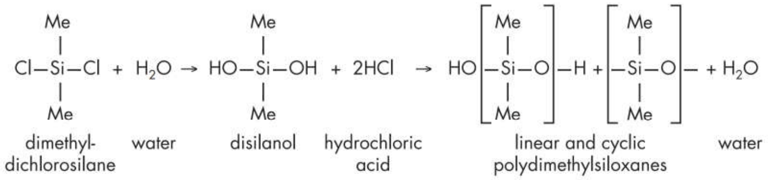

$$Cl-\underset{Me}{\overset{Me}{Si}}-Cl + H_2O \rightarrow HO-\underset{Me}{\overset{Me}{Si}}-OH + 2HCl \rightarrow HO\left[-\underset{Me}{\overset{Me}{Si}}-O\right]-H + \left[-\underset{Me}{\overset{Me}{Si}}-O\right]- + H_2O \qquad \textbf{(EQ 14)}$$

- Some trimethylchlorosilane (Me_3SiCl),
- A small amount of methyldichlorosilane ($MeHSiCl_2$), plus
- Smaller amounts of other silanes.

The chlorosilanes are then separated from one another through the process of distillation.

Chlorosilane Distillation

Distillation is not a reaction. It is a liquid → gas → liquid phase change. Each of the chlorosilanes produced during the synthesis stage has a unique boiling point. These boiling points are used to distill the chlorosilanes from one another based on the number of chlorine atoms attached to the molecule. Once separated, the chlorosilanes are ready to be turned into useful siloxanes through the process of hydrolysis and condensation.

Chlorosilane Hydrolysis and Condensation

When water is added to dimethyldichlorosilane (the principal chlorosilane), the two react to form disilanol and hydrochloric acid. This occurs because oxygen "likes" silicon more than chlorine, and chlorine "likes" hydrogen more than oxygen (see Equation 14).

The disilanols are unstable and strongly attracted to one another. Catalyzed by the hydrochloric acid, they condense into polydimethylsiloxanes—molecules containing a backbone of silicon atoms bonded to oxygen atoms. Hydrolysis and condensation occur spontaneously, simultaneously, and very quickly. These reactions are a veritable "perpetual chemistry machine," resulting in a mixture of

- Cyclic rings (with 3–6 repeating SiO units) and
- Linear chains (with 30–50 repeating SiO units).

The cyclic and linear oligomers (mini-polymers) are separated from one another and distilled into cuts based on the number of SiO units in the chain. Some are used as they are (cyclosiloxane and low-molecular-weight silicone fluids, for example). But the majority are further polymerized and finished to create a wide array of materials with an amazing range of performance capabilities (Dow Corning Corporation 2015).

Fumed Silica

Fumed silica is produced by hydrolyzing silicon tetrachloride ($SiCl_4$) in an oxygen-hydrogen flame at high temperature, resulting in fine SiO_2 primary particles (10–40 nm). The primary particles accumulate and collide in the flame and agglomerate. The agglomerates and the waste gas (hydrochloric acid vapor, HCl(g)) are placed in a high-efficiency gas–solid separator column. The waste gas exits from the top of the separator and goes to a tail gas treatment system. The fumed silica (SiO_2) is removed from the bottom of the separator, into a container, and subsequently packaged. The reaction formula is

$$SiCl_4 + 2H_2(g) + O_2(g) \rightarrow SiO_2 + 4HCl(g) \qquad \textbf{(EQ 15)}$$

Fumed silica is used as an additive in silicone rubbers to increase the strength, as a thickening agent for paints, and an as a desiccant. It is also used in cosmetics, abrasives, and coatings.

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 (e.g., amine, acid, ester, alcohol). The general formula of functional silanes is

$$X_{4-(n+p+q)}\ SiRnR'pR''_q \qquad \textbf{(EQ 16)}$$

R, R′, and R″ are the organic radicals, and X is Cl or OH. The major application for functional silanes is a coupling agent between inorganic and organic compounds, such as inorganic fillers (glass, silica, clays, etc.) in organic matrices (epoxy, polyester, etc.) (Luque and Hegedus 2003).

Polycrystalline Silicon Production

Silicon is a semiconductor and cannot conduct electricity when in a pure (minimal impurities) form, because there are very few free electrons available to carry a current:

	Resistivity, Ω-cm
Conductors	10^{-8} to 10^{-6}
Semiconductors	10^{-6} to 10^{-2}
Insulators	10^{7} to 10^{22}

The electrical conduction properties of silicon can be increased through either of the following methods.

Intrinsic Conduction

Intrinsic conduction is possible through physically heating the silicon. At any temperature above 0 K (–273°C), some of the bonds linking the silicon atoms are broken, resulting in a free electron and an absence of an electron (hole). These free electrons can now conduct electricity and the holes are free to move within the lattice. The magnitude of the number of free electrons based on temperature is as follows:

- At 300 K (27°C), the number of free electrons $= 1.6 \times 10^{10}/cm^3$, and the resistivity = 230,000 ohm·cm
- At 673 K (400°C), the number of free electrons $= 1 \times 10^{17}/cm^3$, and the resistivity = 0.1 ohm·cm

Extrinsic Conduction

Extrinsic conduction is feasible by the addition of trace impurities or "doping" to the silicon. Silicon has four electrons in the valence shell. Group VA (phosphorus, arsenic, and antimony) have five electrons in the valence shell and replace a silicon atom in the crystalline lattice (substitutional), resulting in an extra electron free to conduct electrical current considered "donors" or "n-type" impurities. Elements from group IIIA of the periodic table of elements (boron, aluminum, and gallium) have three electrons in the valence shell and replace

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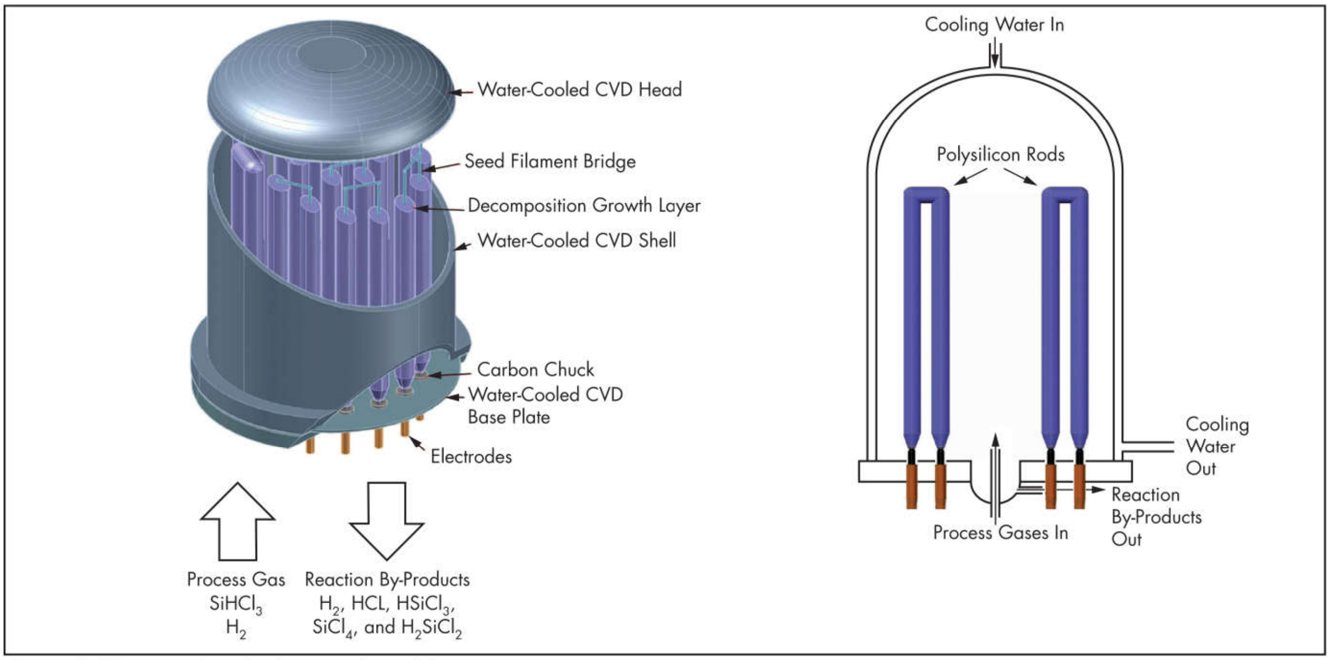

Figure 9 Siemens chemical vapor deposition reactor

a silicon atom in the crystalline lattice (substitutional). Group IIIA elements require an electron to form a bond considered "acceptors" or "p-type." Extrinsic conduction, using acceptors and donors, is the foundation for the creation of silicon-based devices such as computer chips and solar panels.

Many processes developed to produce poly-Si and have been tested, patented, and operated for many years. Three commercial processes make the bulk of the world's current poly production: Siemens, Union Carbide, and Ethyl Corporation. These processes are explained in the following sections.

The Siemens process. The main process steps are as follows:

1. Silicon tetrachloride (STC), hydrogen gas (H_2), and metallurgical silicon (Si) are fed into a fluidized bed reactor. The hydrochlorination process to produce trichlorosilane (TCS) is represented by the following equation:

   $$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl \qquad \textbf{(EQ 17)}$$

   This is followed by the direct chlorination reaction where HCl reacts with raw MG-Si:

   $$3HCl + Si \rightarrow HSiCl_3 + H_2 \qquad \textbf{(EQ 18)}$$

   The hydrochlorination reaction results in approximately 20% TCS conversion at 773 K (500°C), 35 bar, with a 1:1 ratio of STC to H_2 in one pass through a fluidized bed of MG-Si.
2. The TCS produced is then subjected to a double purification through fractional distillation. The first phase is removing the heaviest components resulting from the direct synthesis.
3. The second phase is eliminating the components lighter than TCS, also called volatiles.
4. High-purity TCS is then vaporized, diluted with high-purity hydrogen, and then directed into a chemical vapor deposition (CVD) reactor where the main reaction takes place (Figure 9). The gas is decomposed onto the surface of heated silicon seed rods, electrically heated to about 1,100°C, and growing large rods of ultra-high-purity silicon. The reactions within the CVD reactor include the following:

   $$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4 \qquad \textbf{(EQ 19)}$$

   $$H_2SiCl_2 \rightarrow Si + 2HCl \qquad \textbf{(EQ 20)}$$

   $$H_2 + HSiCl_3 \rightarrow Si + 3HCl \qquad \textbf{(EQ 21)}$$

   $$HCl + HSiCl_3 \rightarrow SiCl_4 + H_2 \qquad \textbf{(EQ 22)}$$
5. The stream of reaction by-products, which leaves the reactor, contains H_2, HCl, $HSiCl_3$, $SiCl_4$, and H_2SiCl_2. These products are recycled back to the front of the hydrochlorination process for further treatment and capture of the silicon.
6. The polysilicon rod products from the CVD reactor are transported to a clean room to be sized, or broken into chunk, and sealed in virgin polyethylene bags that will be sent to silicon ingot producers. The bags contain a precisely weighed amount of polysilicon, typically 5–10 kg product weight (Hunt 1990; Ceccaroli and Lohne 2003).

The Union Carbide process. The main process steps are as follows:

1. The hydrogenation of STC, mixed with H_2 gas through a mass bed of MG-Si, is carried out in a fluidized bed reactor through the following reaction:

   $$3SiCl_4 + 2H_2 + Si \rightarrow 4HSiCl_3 \qquad \textbf{(EQ 23)}$$
2. The TCS is separated by distillation while the unreacted STC is recycled back to the hydrogenation reactor.
3. The purified TCS is then redistributed in two separate stages through fixed bed columns filled with ion exchange

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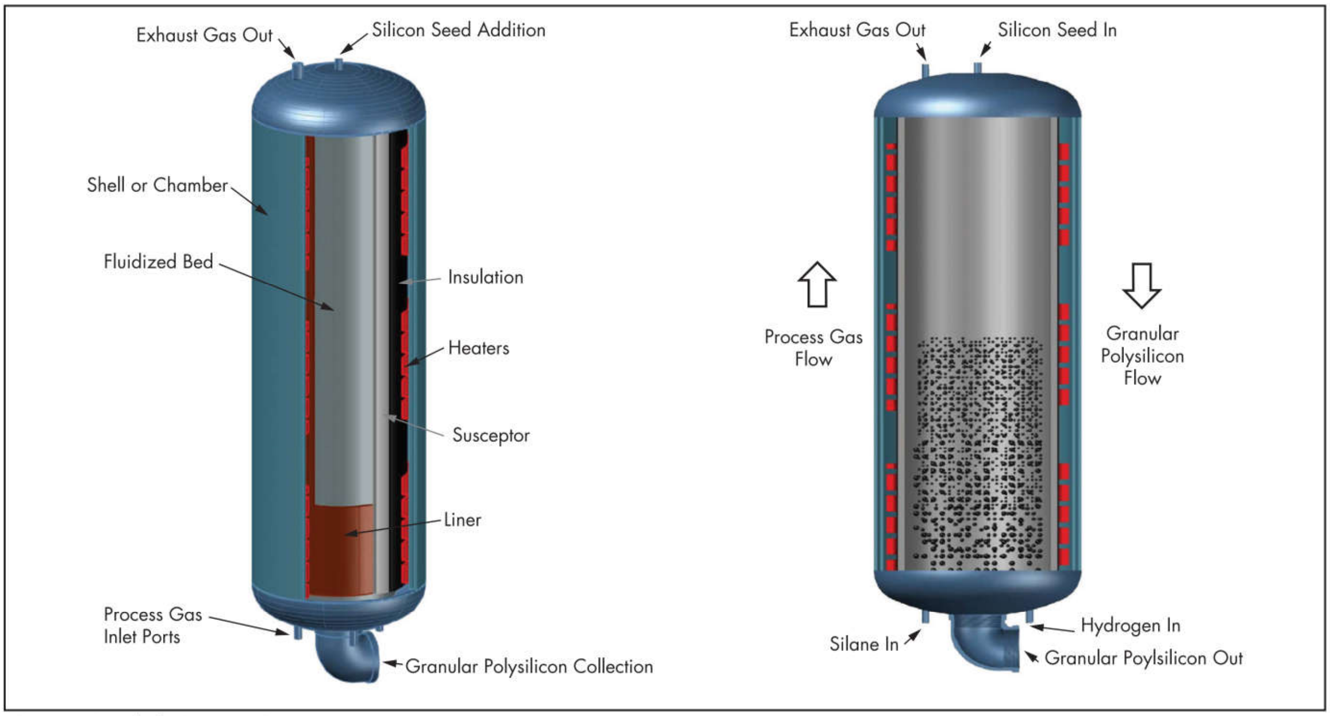

Figure 10 Ethyl Corporation process

resins acting as a catalyst to the following two redistribution reactions:

$$2HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4 \quad \textbf{(EQ 24)}$$

$$3H_2SiCl_2 \rightarrow SiH_4 + 2HSiCl_3 \quad \textbf{(EQ 25)}$$

4. The products of the two preceding reactions are separate distillations. STC and TCS are recycled back to the hydrogenation reactor and the first redistribution stage, respectively.
5. Silane (SiH_4) is further purified by distillation to ultrahigh-purity levels. The silane is then pyrolyzed to produce polysilicon in a Siemens-style CVD reactor by the following reaction:

$$SiH_4 \rightarrow 2H_2 + Si \quad \textbf{(EQ 26)}$$

6. This Union Carbide method produces a measurable amount of amorphous silicon powder due to homogeneous decomposition of silane, and this powder typically adheres to the cooler reactor walls.
7. STC and TCS are recycled and purified many times before conversion to silane, and the results are extremely high-purity silane and subsequent polysilicon.
8. Polysilicon rods produced by the Union Carbide process are strong and typically void-free and are particularly suitable for single-crystal manufacturing by the floating zone method described in a later section. The majority of the product is sized similar to the Siemens process in 5-kg bags (Luque and Hegedus 2003).

The Ethyl Corporation process. The main process steps are as follows:

1. High-purity silicon is produced in the fluidized bed reactor by decomposition of silane in a hydrogen atmosphere by the following reaction:

$$SiH_4 \rightarrow 2H_2 + Si \quad \textbf{(EQ 27)}$$

2. This reaction is exothermic, but additional heat must be provided to balance the thermal losses. Recycled purified hydrogen and silane are introduced continuously through the bottom of the reactor, while high-purity silicon seed particles are introduced through the top of the reactor (Figure 10). The granular polysilicon finished product is cooled and collected through the bottom of the reactor. The hydrogen-rich off-gas is cooled, and the fines are removed, compressed, purified, and recycled back to the reactor. The equipment contact surfaces are typically constructed from high-purity silicon or are silicon coated to maintain purity of the granular silicon.
3. Operating conditions for the reactor are stated as 600–800°C and 5–15 psig. The average particle size for the granular polysilicon is 700–1,100 µm. As with the Union Carbide process, this process produces a measurable amount of amorphous silicon powder due to homogeneous decomposition of the silane (Luque and Hegedus 2003).

Polycrystalline silicon impurities. The purity of silicon produced by the refining operations mentioned previously dictate how it can be used, as photovoltaics, semiconductors, or waste for recycle. Required purity levels are presented in Table 2. Recent efforts to produce photovoltaics from upgraded MG-Si have produced good results from less restrictive purity requirements and at less cost (Søiland et al. 2012).

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Table 2 Polycrystalline silicon impurities

Attribute		Grade	
		Photovoltaic	Semiconductor
Purity	Boron, B	≤3 ppba	≤0.1 ppba
	Donors: P + As	≤5 ppba	≤0.2 ppba
	Carbon	≤1 ppma	≤0.2 ppma
Surface metals	Aluminum, Al	<5 ppbw	<0.6 ppbw
	Cobalt, Co	—	<0.6 ppbw
	Copper, Cu	<2 ppbw	<0.1 ppbw
	Chromium, Cr	<2 ppbw	<0.2 ppbw
	Iron, Fe	<10 ppbw	<0.8 ppbw
	Nickel, Ni	<2 ppbw	<0.2 ppbw
	Potassium, K	—	<0.5 ppbw
	Sodium, Na	<5 ppbw	<0.5 ppbw
Bulk metals	Total	<30 ppbw	<2 ppbw
Packaging	Virgin polyethylene bags	5 or 10 kg ±0.5%	5 kg ±0.5%

SILICON INGOT PRODUCTION METHODS

To produce high-quality silicon ingots, the distribution of impurities must be determined. The equilibrium segregation coefficient (k_o) is the ratio of the concentration of the impurity in the solid silicon (C_S) and the bulk liquid silicon (C_L):

$$k_o = C_S / C_L \qquad \textbf{(EQ 28)}$$

Table 3 contains the equilibrium segregation coefficient for various impurities in silicon. Equilibrium segregation coefficients are only pertinent if the ingot growth rate is very low, such as with the directional solidification system.

If the equilibrium segregation coefficient is much lower than 1, then the impurity will most likely stay in the molten silicon and end up in the top layer of the ingot, or will be the last section to solidify.

For processes that are carried out at a rate which would not allow the pickup of impurities under true equilibrium conditions, the distribution of impurities in the liquid and the solid would depend on the effective segregation coefficients (k_{eff}).

Table 3 The equilibrium segregation coefficient for various impurities in silicon

Impurity	Ta	Ag	Fe	Co	Ti	Mn
Equilibrium segregation coefficient	1×10^{-7}	1×10^{-6}	8×10^{-6}	8×10^{-6}	2×10^{-6}	4.5×10^{-5}
Impurity	**Ni**	**Au**	**Zn**	**S**	**Cu**	**In**
Equilibrium segregation coefficient	3×10^{-5}	2.5×10^{-5}	1×10^{-5}	1×10^{-5}	4×10^{-4}	4×10^{-4}
Impurity	**Al**	**Ga**	**Sn**	**Sb**	**C**	**Ge**
Equilibrium segregation coefficient	0.002	8×10^{-3}	0.016	0.023	0.08	0.33
Impurity	**P**	**B**	**O**			
Equilibrium segregation coefficient	0.35	0.8	1.2			

Source: Davis et al. 1980; Trumbore 1960; Shimura 1989

The following equations are used for calculating the effective segregation coefficient (Shimura 1989):

$$k_{eff} = k_o / [k_o + (1 - k_o) \exp(-G_s \sigma / D)] \qquad \textbf{(EQ 29)}$$

$$\sigma = 1.6 D^{1/3} \nu_k^{1/6} \omega^{-1/2} \qquad \textbf{(EQ 30)}$$

where

k_{eff} = effective segregation coefficient
k_o = equilibrium segregation coefficient
G_s = solidification rate
σ = diffusion layer thickness
D = diffusion coefficient of impurity in the melt
ν_k = kinematic viscosity of liquid
ω = relative rotation of the crystal

The effective segregation coefficient is usually determined experimentally, due to the difficulty determining the diffusion layer thickness (Schei et al. 1998).

Directional Solidification System for Multicrystalline Ingots

Multicrystalline ingots are produced via directional solidification of silicon in quartz crucibles:

1. Electronic-grade polysilicon is melted in a quartz crucible at a temperature >1,673 K (>1,400°C) in an argon gas atmosphere by a resistance or induction heater. The silicon melt temperature is kept above the silicon melting point.
2. The silicon seed product is placed in the bottom of the crucible during loading and acts as a starting point for the large grain formation.
3. The ingot is solidified from the bottom to the top by moving the crucible down through the heater, or moving the heater up past the crucible, or using induction heating and turning of power sequentially from the bottom coils to the top coils.
4. As the process continues, all silicon in the crucible freezes, and the impurities are collected on the top surface (see Figure 11).

Czochralski Zone Puller for Single-Crystal Rods

The Czochralski method is a technique to pull a single crystal with the same crystallographic orientation of a small monocrystalline seed crystal out of melted poly-Si (Figure 12).

1. Electronic-grade poly-Si is melted in a quartz crucible at a temperature >1,673 K (>1,400°C) in an argon gas atmosphere by a graphite heater. The temperature of the silicon melt is kept above the silicon melting point.
2. A monocrystalline silicon seed crystal is immersed into the melt and acts as a starting point for the crystal formation. A thin "dashed neck" is established between the seed and the ingot to reduce dislocations from freezing.
3. The seed crystal is slowly pulled out of the melt, where the pull speed determines the crystal diameter. During crystal growth, the crystal as well as the crucible counter-rotate to improve the homogeneity of the crystal.
4. Before the crystal growth is finished, a continuous increase of the pull speed reduces the crystal diameter toward zero. This helps prevent thermal stress in the ingot that could happen by an abrupt lifting out of the melt, rapidly reducing the ingot temperature, which can destroy the crystal.

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Float Zone Method

The float zone (FZ) method is a technique to pull a single crystal with the same crystallographic orientation of a small monocrystalline seed crystal out of melted polysilicon rod using a radio-frequency coil as the heat source.

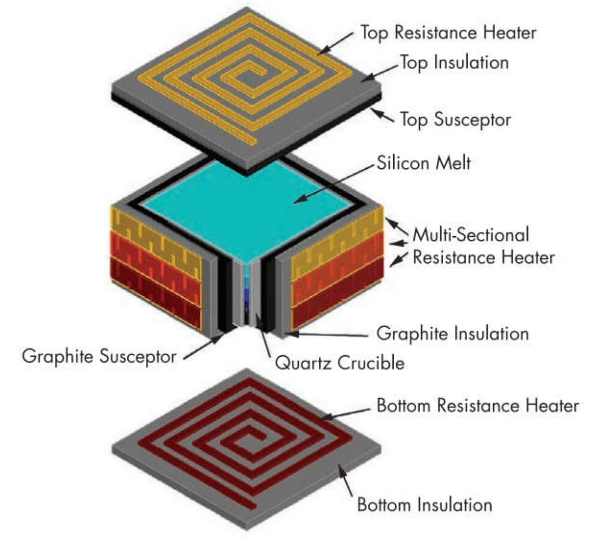


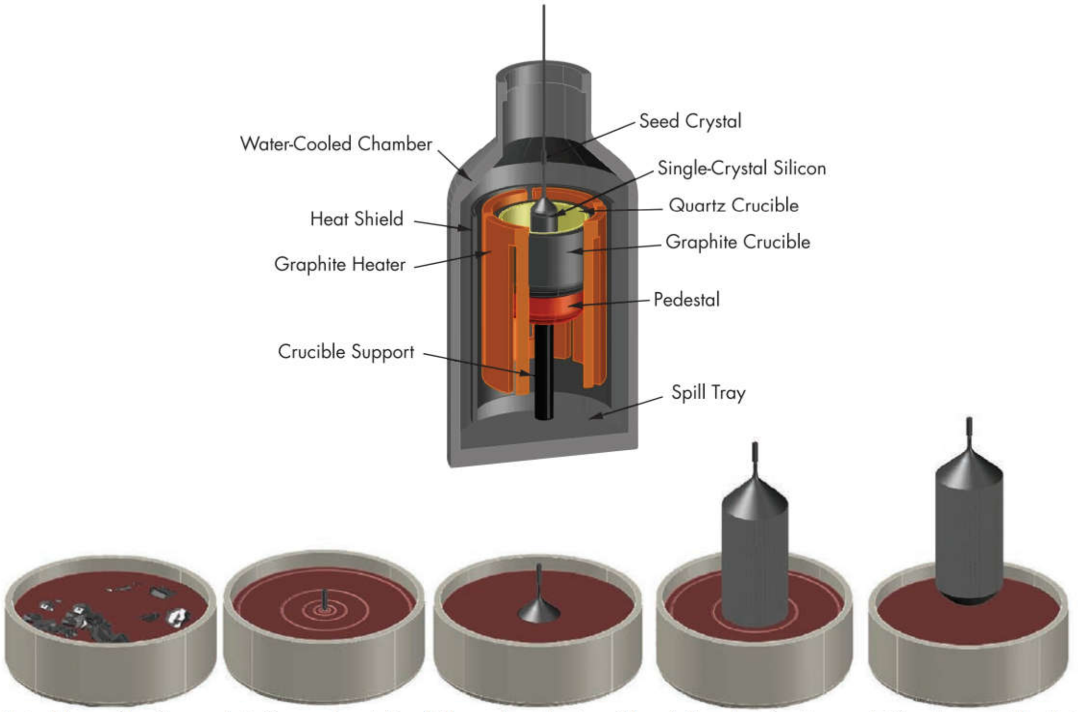
Figure 11 Directional solidification system

1. The FZ method starts with a high-purity polycrystalline rod and a monocrystalline seed crystal that are held face to face in a vertical position and are rotated countercurrently (see Figure 13).
2. A radio-frequency coil is placed around the poly-Si rod and a molten area is established. The seed is brought up from below to contact the drop of melt formed at the tip of the polysilicon rod. A necking process is carried out to establish a dislocation-free crystal before the neck is allowed to increase in diameter to form a taper and reach the desired diameter for steady-state growth.
3. As the molten zone is moved along the poly-Si rod, the molten silicon solidifies into a single-crystal ingot. FZ crystals are doped by adding the doping gas phosphine (PH_3) or diborane (B_2H_6) to the inert gas for n- and p-type, respectively.

Finished silicon ingots are shipped to wafer fabricators and device manufacturers for further processing. Multicrystalline ingots are used exclusively for solar cells while the main end user for single-crystal ingots is the semiconductor industry.

SAFETY CONSIDERATIONS

Caution is required when producing the chemicals and metals that are described in this chapter. Chlorine chemistry is the basis of the reaction chemistry, beginning with the feedstock that is used. Silicon tetrachloride (STC, $SiCl_4$) is highly toxic, producing hydrochloric acid vapor (HCl) when it is exposed to air. HCl vapor is lethal to most life forms. Intermediate products that are produced during the production of silicones



1. Load the crucible with polysilicon and heat to melting temperature.
2. A silicon seed crystal is introduced to the top of the melt.
3. The seed crystal and crucible rotate in opposite directions as the pull seed is adjusted to create a single-crystal cone with a "dashed neck."
4. A constant-diameter single-crystal section is created by adjusting the pull seed and the rotation.
5. Once the targeted length is achieved, the single-crystal ingot is raised for cooling.

Figure 12 Czochralski zone puller for single-crystal ingots

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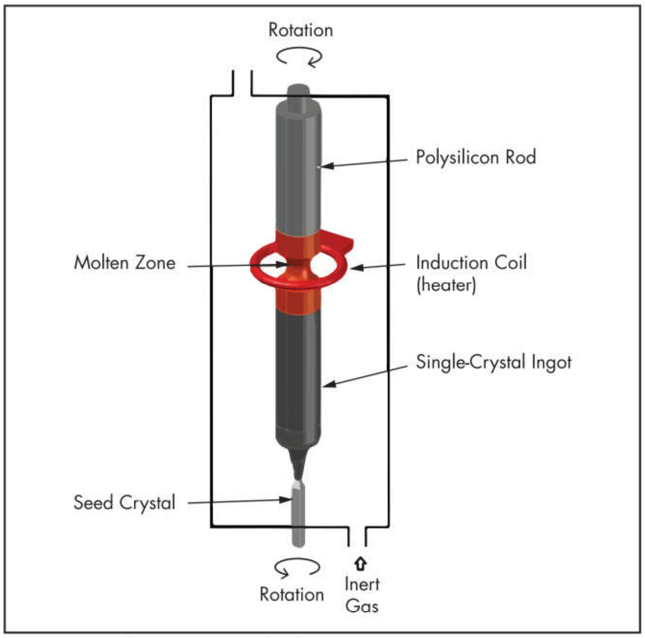

Figure 13 Float zone method

and high- and ultra-high-purity silicon are chlorine-based chemicals—that is, trichlorosilane (TCS, $HSiCl_3$), dichlorosilane (DCS, H_2SiCl_2) and monochlorosilane (MCS, H_3SiCl)—and these chemicals will also produce hydrochloric acid upon exposure to air. Care must be used in handling any of these chemicals.

Silane (SiH_4) can autoignite at temperatures under 327 K (54°C). Regrettably, it has been the cause of injuries and deaths. Extreme care is essential in handling of the gas.

Additionally, when designing processes to treat these chemicals, proper material selection is required to contain the chemicals. Intense mechanical integrity programs using sophisticated nondestructive examination techniques must be applied to ensure that the processes remain safe after processing has been intimated.

Safety concerns are also associated with silicon metal dust that is part of the feed used in the fluid bed reactors that produce silicon-based chemicals. Three processes that are commonly used in the preparation of silicon metal for fluid bed reactors are crushing, to produce the required sizes for use in the fluid bed reactors; pneumatic conveyance, for moving the sized product to storage from the crusher and then from the storage bins to the various reactors; and dust handling, to capture the small particles of dust in baghouses, cyclones, or dry scrubbers. If the following conditions exist at the same time, the metal dust can be highly explosive:

1. Correct particle sizing (<60 µm)
2. Correct concentration of silicon metal dust and air
3. Oxygen levels greater than 8%
4. An energy source of sufficient magnitude

Explosions in facilities that contain these processes have been damaged beyond repair and, unfortunately, human lives have been lost. Removal of any one of the preceding four conditions eliminates the potential occurrence of an explosive condition. Therefore, nitrogen gas is typically used to inert operations and maintain very low levels of oxygen to keep these operations in the reduced state and safe.

Finally, pressure relief devices, also referred to as safety valves, are required and used on any and all vessels that are used to contain, store, and feed the chemical plants that produce these products. The utmost of care must be used while handling silicon metal products and the chemicals produced in the manufacture of these products.

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