

Solar Grade Silicon Feedstock

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5.1 INTRODUCTION

The Photovoltaic (PV) industry is still in its infancy and at the moment it is very difficult to predict which technical, economical and social patterns its deployment will follow before reaching maturity. However, if photovoltaics are to become a major energy source in the future, it is appropriate to question which materials and which natural elements are critical to secure the long-term sustainability of this energy source. This is particularly valid for the semiconductor materials whose band gap has to perform the efficient conversion of sunlight to electricity. The recent history of photovoltaics (from the 1950s) reveals an intense activity of research and development embracing a broad range of disciplines and leading to a healthy multitude of innovations. Organic versus inorganic semiconductors, intrinsic versus extrinsic semiconductors, homojunctions versus heterojunctions and amorphous versus crystalline structures are a few dilemma that new research achievements steadily bring to the scientific and industrial community. It will take years, perhaps decades, before mankind is able to solve the challenge and answer the questions addressed above. (These aspects are also described in Chapters 6 to 16 of this handbook.)

Up to now, the dominant semiconductor material used in photovoltaics is silicon, particularly crystalline silicon. The most recent market surveys issued by commercial consultants, (trans)governmental organisations and agencies clearly state this fact.¹ Analysing annual growth by means of technology and material from these quoted sources, multicrystalline silicon takes the lion's share of the growth. In the first half of the 1990s,

¹ For PV News edited by Maycock (2001), commercial shipments to terrestrial and indoor applications of cells or modules based on non-silicon technologies accounted in 2000 for just 1.2 MW of a total 288 MW, that is, 4.2 per thousand. Amorphous silicon was credited in the same period 27 MW shipment or 9.4% and crystalline

multicrystalline sawn wafers accounted for just half of the single-crystal shipments. In 1998 both technologies were equivalent in size. Two years later, multicrystalline technology surpassed single-crystal technology by 55%.

The consensus is that crystalline silicon is and will remain for at least a long decade the workhorse of this growing market. Long-term visionary forecasts predict that by 2050, 30 000 TWh PV electricity will be generated annually worldwide. This will require an installed PV output capacity totalling approximately 15 million metric tons (MT) of solar grade silicon feedstock, assuming that silicon remains dominant and that cell efficiency and material yields have steadily improved. To build up such a capacity over fifty years will represent an annual production of 300 000 MT solar grade silicon feedstock. The annual present consumption of pure silicon for photovoltaics is approximately a hundredth part of that (i.e. 4000 MT), whereas production of metallurgical grade silicon for all purposes in 2000 was approximately one million metric tons. This clearly poses the question of material feasibility and availability. The present chapter is therefore dedicated to silicon, its extraction, purification and availability by current and future practice.

5.2 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 26% of the Earth's crust and is the second most abundant element in weight, oxygen being the largest.

5.2.1 Physical Properties of Silicon Relevant to Photovoltaics

Silicon is a semiconductor with a band gap E_g of 1.12 eV at 25°C. At atmospheric pressure, silicon crystallises into a diamond cubic structure, which converts into a body-centred lattice when subjected to ca 15 GPa. Under some circumstances, slow-growing

silicon the balance, that is, close to 90% of which 49% (141 MW) are cells made of multicrystalline sawn wafers, 31% (90 MW) of single-crystal wafers and 10% (28 MW) are cells based on various crystalline silicon technologies, for example, ribbon (15 MW or 5.1%), amorphous silicon on single-crystal silicon slices (12 MW or 4.2%) and others (approx. 1 MW or 3.5 per thousand).

Solar Modules Shipment by Technology (Source: PV News 2001)

Technologies	Shipped output in 2000
Amorphous silicon	27 MW (9%)
Single crystal silicon wafers	90 MW (31%)
Multicrystalline sawn silicon wafers	141 MW (49%)
Various crystalline silicon technologies (i.e. ribbon, films, amorphous on single crystal)	28 MW (10%)

Other sources available in May–November 2001 at the time of writing this chapter, such as the German magazine Photon International March 2001 published congruent data for the same period. Statistics from non-commercial entities as those edited by the International Energy Agency (IEA-PVPS programme) covering 21 industrialised countries, members of the OECD-organisation, show over years the same trends [1–4].

faces of silicon are (111) but in epitaxial films and polysilicon deposition (111) is the fastest growth direction. Vapour deposition below 500°C results in amorphous silicon. If reheated above this temperature, crystallisation will occur.

Unlike most of the compounds and elements, silicon contracts when melting or expands when solidifying.

Impurities incorporated in the silicon lattice during the crystal growth or during the post-treatment (diffusion, implantation etc.) ionise at low temperatures, thus providing either free electrons or holes. Impurities from the Group IIIA replace a Si atom in the atomic lattice to supply electrons and are called *n*-dopants or donors, whereas elements from the Group VA substitute for a Si atom to supply holes and are called *p*-dopants or acceptors (see Section 5.6.3). Phosphorus and boron represent these groups and are used in PV processing to control the semiconductor properties (doping levels) of silicon. Impurity concentrations are expressed in atoms of impurity per cubic centimeter of the host material (silicon). In silicon semiconductor devices, these vary from 10^{14} to 10^{20} atoms per cm^3 and can be directly measured by analytical instruments. An indirect measure of impurity concentration is the minority-carrier lifetime. This is the time that elapses before a free electron in the lattice recombines with a hole. The transition metals, Fe, Cr, Ni, degrade the minority-carrier lifetime and the solar cell performance. High-purity silicon crystals with metal content less than 10 ppb(w) have minority-carrier lifetime values as high as 10 000 μs . Semiconductor wafers with phosphorus and boron dopants have values from 50 to 300 μs . Solar cells require minority-carrier lifetime value of at least 25 μs .

The relatively high refractive index limits the optical applications of silicon. The absorption/transmission properties in the 0.4 to 1.5 μm wavelength spectra are important in the performance of PV cells and photoconductive devices. In PV applications antireflective layers applied to silicon are commonly used.

Silicon even when alloyed with small quantities of impurities is brittle. Shaping silicon for PV applications requires sawing and grinding. Microelectronic applications require polishing. These mechanical operations are very similar to those applied to glasses.

Various thermal and mechanical properties are reported in Table 5.1.

For more details the reader is invited to consult the References [5–8].

Table 5.1 Thermal and mechanical properties of silicon

Property	Value
Atomic weight	28.085
Atomic density (atoms/ cm^3)	5.0×10^{22}
Melting point ($^{\circ}\text{C}$)	1410
Boiling point ($^{\circ}\text{C}$)	2355
Density (g/cm^3 at 25 $^{\circ}\text{C}$)	2.329
Heat of fusion (kJ/g)	1.8
Heat of vaporisation at MP (kJ/g)	16
Volume of contraction on melting (%)	9.5

5.2.2 Chemical Properties Relevant to Photovoltaics

Silicon is stable in the tetravalent state and has a strong affinity for oxygen, forming stable oxides and silicates, the only natural occurrences known for silicon. Artificially isolated elemental silicon immediately oxidises, forming a thin protective film of silica of less than 100 Å, which prevents further oxidation. Oxygen plays an important role in silicon-semiconductor devices, for instance, in manufacturing metal oxide semiconductor (MOS) transistors.

Silicon and carbon (Group IVA) form a strong Si–C bond and stable products. Silicon carbide is artificially synthesised in several allomorphic structures, finding various applications in photovoltaics and electronics. Primary uses are the abrasive properties of SiC for wafering silicon crystals and the emerging applications of SiC semiconductors. The strong Si–C bond is also the origin of the rich organosilicon chemistry encompassing numerous polysiloxanes (commonly named *silicones*) and organosilanes in which organic radicals are attached to silicon atoms through a covalent Si–C bond.

The tetravalence and the similarity of silicon and carbon are illustrated in the ability of silicon to form bonds with itself, Si–Si, and to form polymers, for example, $-(\text{SiH}_2)_p-$, $-(\text{SiF}_2)_p-$, comparable to hydrocarbons and fluorocarbons, although the length of the chains remains modest in the case of the silanes.

Silicon forms hydrides; Monosilane (SiH_4) is a key chemical compound for the production of amorphous silicon and the purification of silicon to semiconductor grade (see later in this chapter).

The chemical reactivity of silicon with chlorine is also extremely important. Alkyl- and arylchlorosilanes are the necessary intermediates to build the polysiloxane chains (silicones). Trichlorosilane and tetrachlorosilane, because they are volatile at low temperature and can be decomposed to elemental silicon at high temperature, are both the intermediates and the by-products of the purification processes upgrading metallurgical grade silicon to semiconductor purity (see later in this chapter). Other chlorosilanes or halogenosilanes are also used in chemical vapour deposition applications. The halogen atom is easily substituted by a hydroxyl group, $-\text{OH}$, through hydrolysis. Such a hydroxyl group tends to react with other functional groups by exchanging the hydrogen atom. This is the basis of a rich surface chemistry.

Silicon and germanium (Group IVA) are isomorphous and mutually soluble in all proportions.

Tin and lead, also elements of Group IVA, do not react with silicon and are not miscible in silicon, which is mentioned as a remarkable curiosity.

For more details on the chemical properties the reader is invited to consult the References [8–11].

5.2.3 Health Factors

The surface of elemental silicon is oxidised and is relatively inert and is considered as non-toxic. Hazard risks with elemental silicon are high when silicon occurs as a fine

powder in the presence of an ignition source. Damaging and fatal explosions have been reported by the silicon industry. The raw material, from which silicon is made, quartz or quartzite, is one of the sources of silicosis. Most of the hazards are related when quartz/quartzite is quarried, exposure taking place during drilling, crushing, loading and bulk handling. Several protection methods must be applied to the quarries and to the metallurgical plants to prevent silicon dust explosion and silicosis. Volatile silanes such as monosilane and chlorosilanes are extremely reactive in the presence of oxygen, water or moisture. They are also classified as hazardous chemical substances whose handling requires special care. Saturated long chain silanes, polysiloxanes as well as amorphous silica are known to be chemically inert and not toxic. Because of that they are widely used in pharmacy, food industry and cosmetics.

The production of metallurgical silicon and electronic grade silicon has an environmental impact through energy consumption, associated with climatic and polluting gases principally CO_2 , NO_x and SO_2 . However, it must be noticed that the corresponding nuisances and energy consumption involved in manufacturing and installing PV systems are “paid back” by the same system in the form of emission-free “green” electricity only after about four to five years of an average existence of more than 25 years. More quantified examples about environmental and energy “payback” are reported from Europe, Japan and Australia and commented in [12].

5.2.4 History and Applications 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 12000 B.C. Elemental silicon was prepared for the first time in 1824 by Berzelius, 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 trade organisations) was not current until the Second World War. Three major applications have since greatly stimulated the production and purification of silicon, that is, 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

Table 5.2 Chemical characteristics of commercial metallurgical grade silicon

Element	O	Fe	Al	Ca	C	Mg	Ti	Mn	V	B	P
Low (ppm)	100	300	300	20	50	5	100	10	1	5	5
High (ppm)	5000	25 000	5000	2000	1500	200	1000	300	300	70	100
Element	Cu	Cr	Ni	Zr	Mo						
Low (ppm)	5	5	10	5	1						
High (ppm)	100	150	100	300	10						

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. One may find three dozens of companies producing and marketing silicon metal, most of the plants having an annual output of 20 000 to 60 000 MT (see production of silicon metal later in this chapter). The chemical characteristics of commercial metallurgical grade silicon are indicated in Table 5.2.

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.

5.2.4.1 Applications 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.

5.2.4.1.1 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.

5.2.4.1.2 Wrought alloys

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

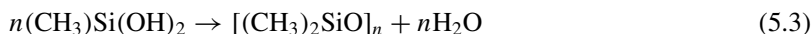
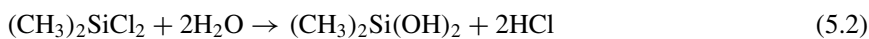
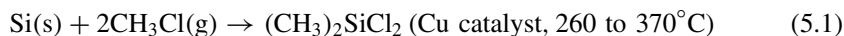
The alloys of the 6xxx series have good hot-working properties and are age-hardening. These alloys are therefore well suited for extrusion of profiles, which by heating at 150 to 200°C are given their final strength.

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

5.2.4.2 Applications in chemistry

5.2.4.2.1 Silicones

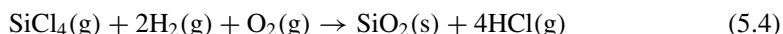
Since the discovery of the direct synthesis (reaction 5.1) of dimethyldichlorosilane, during the Second World War independently by Rochow and Müller, the silicones industry has developed to become a strong and growing chemical business consuming (year 2000) about 400 000 MT of silicon [8–11].



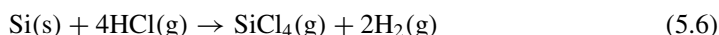
The direct synthesis (5.1) is industrially performed in a fluidised bed reactor requesting small particles or powder of silicon (20–300 µm). The reaction is exothermic and needs to be activated with copper catalysts as well as promoters Zn, Sn, P and others. Whereas Fe does not seem to play an important role, Ca and Al have shown to take an active part in the overall reaction.

5.2.4.2.2 Synthetic silica

Varieties of synthetic silica such as pyrogenic silica (also called *fumed silica*) or silica ingots as feedstock to optical fibres are industrially prepared by burning silicon tetrachloride:



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:

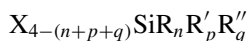


The present fumed silica market is about 100 000 to 120 000 MT, which in turn consumes around 50 000 to 60 000 MT of metallurgical silicon. It is noted that the main market for

fumed silica is as additives in silicone rubbers used to increase the mechanical strength and the elasticity of these elastomers.

5.2.4.2.3 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.

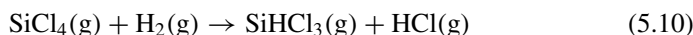
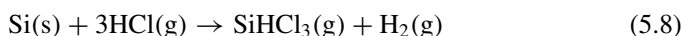


represents a general formula of functional silanes, in which R, R', R'' are organic radicals and X is Cl or OH. There exist a multitude of functional silanes. One of their major applications is as coupling agent between inorganic and organic compounds, for example, inorganic fillers (glass, silica, clays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

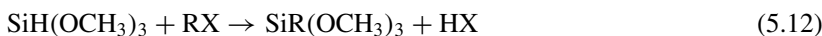
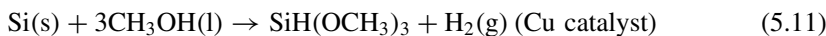
Several routes may be imagined to generate such molecules. The current industrial praxis dictated by economical efficiency is the functionalisation of trichlorosilane according to



whereas trichlorosilane is produced by a direct synthesis in a fluidised or fixed bed reactor:



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 SiCl_4 or by direct reaction of ethanol with silicon in the presence of a catalyst following the same pattern as (5.7) and (5.12).

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

5.2.4.3 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 adequate semiconductor properties is industrially prepared through the distillation and the thermal decomposition of volatile silicon compounds, for example, trichlorosilane, SiHCl_3 , and monosilane, SiH_4 . These operations are performed in large chemical plants, which for synergy reasons 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.

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, aluminium at 2 to 3% and silicon metal overall at 4%.

The present raw material for all silicon solar cells originates from this route. Therefore, a more detailed description of these processes will be given later in the present chapter.

5.2.4.4 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 resistant properties, alloys rich in silicon 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.) [7].

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

5.3 PRODUCTION OF METALLURGICAL GRADE SILICON

5.3.1 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, practical execution 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 concomitant to higher degrees of raw material utilisation.

The furnace consists essentially of a crucible 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. The metallurgical coal is co-produced with coal used for crude steel production. As a rule this coal needs to be washed in order to remove most of the ash containing unsuitable impurities. Raw materials, both quartz and carbon, are selected in order to achieve high product quality (silicon and silica fumes), to maximise furnace performances and to minimize the environmental damages (i.e. SO_2 and NO_x emissions). 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 tip 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.

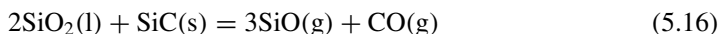
Electrodes are also made of carbon. Originally, expensive graphite electrodes were used. They were displaced by pre-baked electrodes, which in turn tend to be replaced by more cost-efficient self-baking electrodes. The electrode technology is an important aspect to the present development of this industry: 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. The reaction co-product, carbon monoxide $\text{CO}(\text{g})$, is further oxidised to carbon dioxide $\text{CO}_2(\text{g})$ in open furnaces and released into the atmosphere. In open furnaces, side-reactions leading to the formation of silica fumes play an important role for the overall economics of the process:



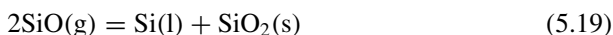
The silica fumes, which consist mainly of very fine particles of amorphous silica less than 1 μm , are passed through filter cloths installed in large bag-house systems adjacent to the furnaces. The collected amorphous finely divided silica finds valuable applications as additives in concrete and refractory. 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.

Reactions (5.13) to (5.15) are a simplification of the complex system. Several main principles can be understood from a more detailed description of the chemistry. There are two important intermediate compounds: the gaseous silicon monoxide SiO(g) as already mentioned in reaction (5.14) and the solid silicon carbide SiC(s) . To interpret the chemistry 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 absolutely indispensable for further reduction according to reaction (5.17).

In the outer zone, where temperature is below 1900°C, SiO(g) and CO(g) convected away 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 $\text{SiO}_2(\text{s,l})$ are formed as the partial pressure of SiO(g) drops:



A schematic description of the furnace is given in Figure 5.1.

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 continuously, or 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.

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%

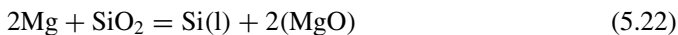
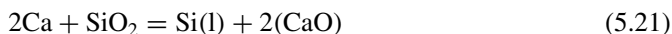
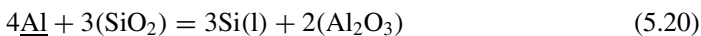
Ti: 0.1–0.02%

C: 0.1–0.15%

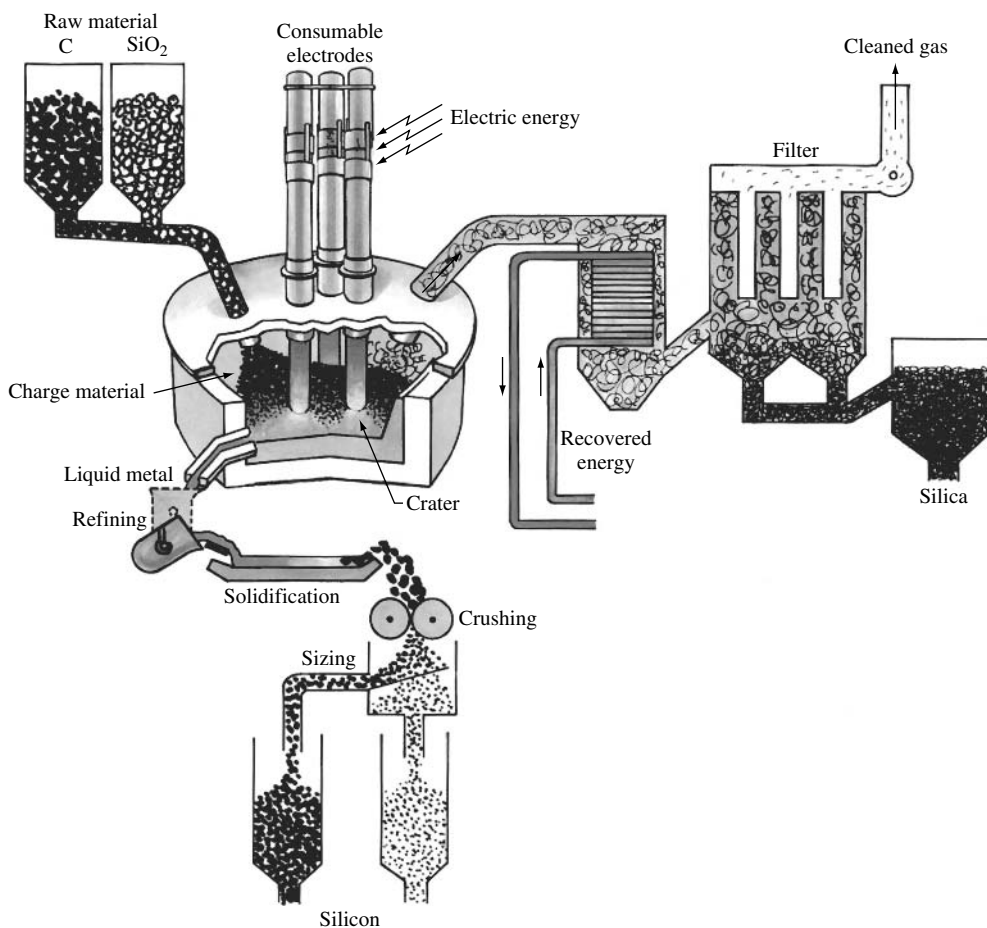
5.3.2 Refining

Most of the applications of silicon as described above request 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 (SiO_2) and lime/limestone (CaO/CaCO_3). Other chemicals such as dolomite (CaO-MgO), calcium fluoride (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 oxidised and

the degree of refining is determined by distribution equilibria (5.20) to (5.23), where the (parentheses) refer to components dissolved in a slag phase and the underscored symbols refer to dissolved elements in liquid silicon:

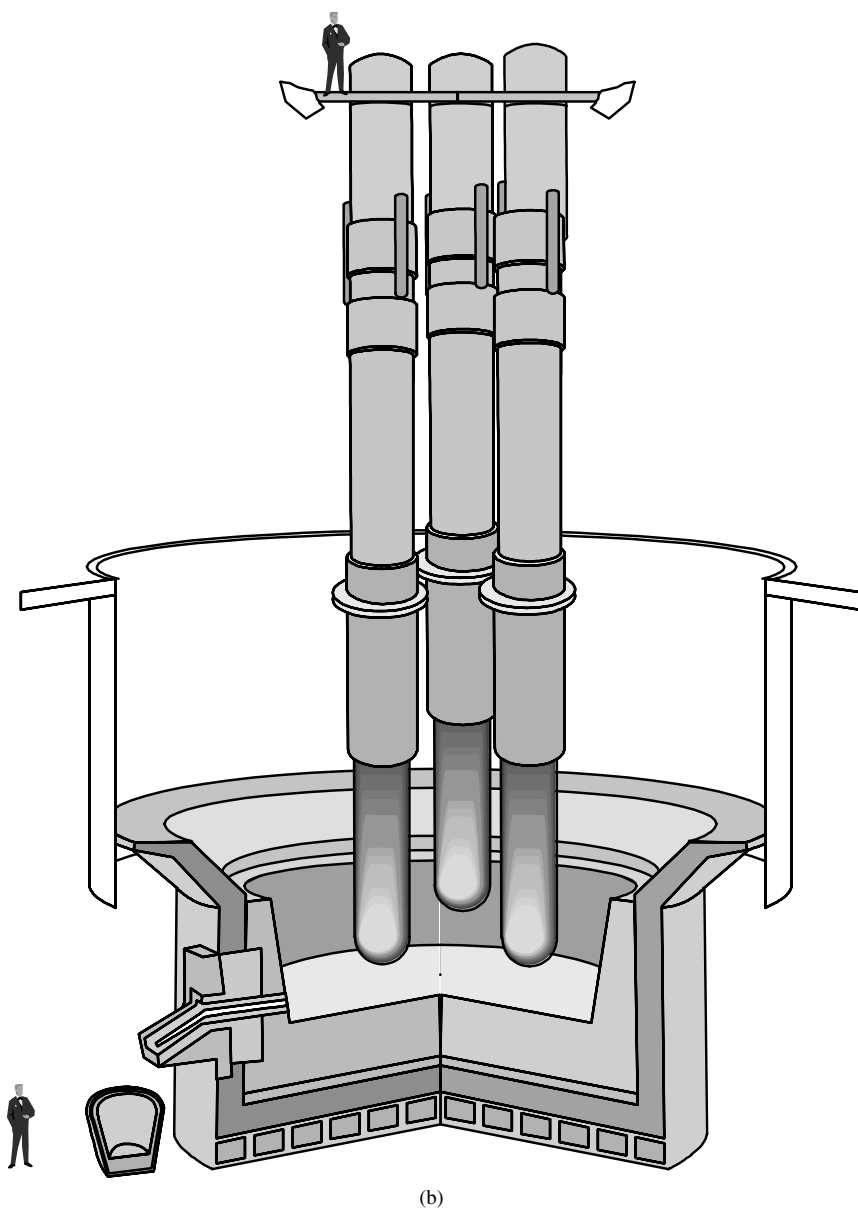


Theoretically it is possible to remove Al and Ca to very low levels, but in practice this is prevented by the large heat losses occurring during this operation. Temperature drops to 1700 to 1500°C, and to avoid freezing of the melt, some of the silica needed for slag



(a)

Figure 5.1 (a) and (b) 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) with permission by Halvard Tveit

**Figure 5.1** (continued)

formation is provided by direct oxidation of Si(l) with added oxygen (oxygen is added to heat silicon to keep it liquid). A disadvantage of this operation is also a partial oxidation of silicon resulting in expensive material losses.

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. For instance, a high CaO content will lead to a low viscosity slag, which will sink to the bottom of the ladle, while CaF will increase the viscosity. 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 [13].

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 efficiently captured by the slag phase and thus are removed from liquid silicon during the ladle treatment and the subsequent pouring. SiC is removed simply by mechanical separation, precipitated particles sticking to the walls of the ladle and the other devices containing the liquid silicon [14]. Dissolved carbon in the range of 80 to 100 ppm(w) 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 later in the present chapter.

5.3.3 Casting and Crushing

The refined melt is poured from the ladle into a cast iron mold or onto a bed of silicon fines. The casting should preferably be removed from the mold while bleeding, that is, not fully solidified. After solidification in standard industrial conditions, metallurgical grade silicon is multicrystalline. 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 [10]. 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 [15]. Oxides and carbides are found as inclusions located at the grain boundaries and to a lesser degree inside the Si grains.

To be used in customers' processes, solidified silicon needs to be further crushed down to small lumps up to 100 mm. This is performed in jaw crushers and roll crushers, since 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. The dominant fracture mode was found by Forwald *et al.* [7, 16] to be transgranular. 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 of the impurities and intermetallic phases. Granulation in water, resulting in small granules of a few millimeters and thus avoiding casting and subsequent coarse crushing, has become a standard practice for several producers [17–19]. In an earlier attempt to avoid casting, crushing and milling, gas atomisation was tested by producers and users, but was not further industrialised for economical reasons [20, 21].

5.3.4 Economics

The carbothermic reduction of quartz in the submerged arc furnace consumes large amounts of energy and material. Best industrial performances are 10 to 11 MWh per metric ton (MT) of silicon metal and 90% silicon yield. Both availability and price of electrical power and raw material such as quartz and coal are therefore extremely sensitive to the silicon metal economics. Boardwine *et al.* [22] have presented the average structure for direct cost for Western producers as follows:

Reduction materials (as coal)	20%
Quartz	9%
Electrodes	12%
Electric power	21%
Supplies and equipment	16%
Labour	17%
Transport (to customers)	5%

In spite of dramatic changes and improvement for the individual producers, particularly with the development of new electrode technologies, the above figures are probably still valid for a large group of plants.

Most of the silicon plants are 20 years or more old. New capacity has been added during the past 10 years mainly by converting ferrosilicon furnaces to silicon. High capital expenditure is a barrier to new expansion. Investment of one million US dollars per one thousand MT of silicon is proposed as an indicating information for new furnaces.

A general and detailed source of information on production of metallurgical grade silicon is found in the recent book *Production of High Silicon Alloys* by Schei *et al.* [23].

5.4 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 hyperpure elemental silicon by reductive pyrolysis or chemical vapour 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. 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 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.

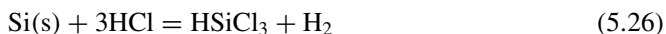
3. Finally, in the third process, also making use of monosilane SiH_4 , the heated silicon rod in the closed reaction chamber has been replaced by a fluidised bed of heated silicon particles. The particles act as seeds on which SiH_4 is continuously decomposed to larger granules of hyper-pure silicon. 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.

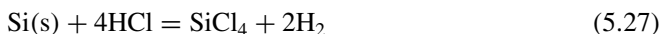
5.4.1 The Siemens Process

A schematic overview of the process is given in Figure 5.2.

Trichlorosilane HSiCl_3 is prepared by hydrochlorination of metallurgical grade silicon in a fluidised bed reactor:



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



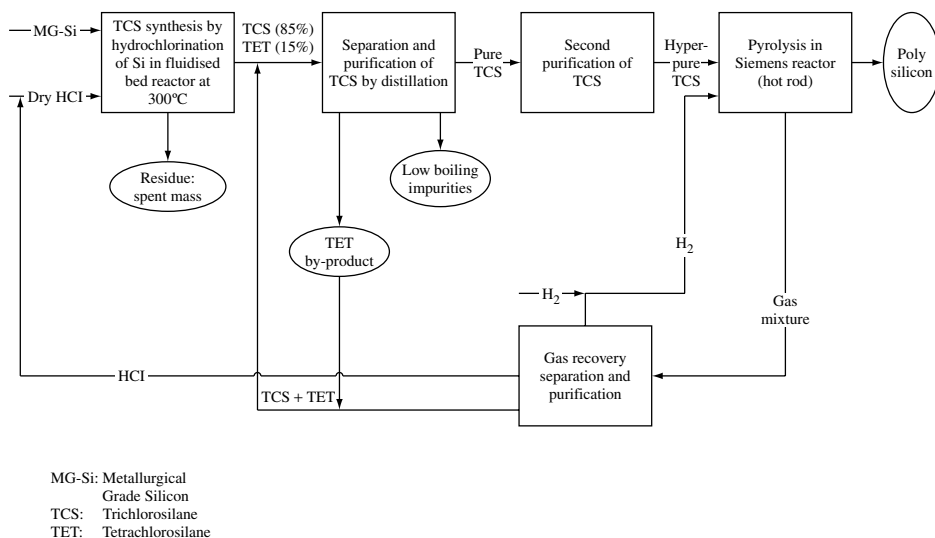


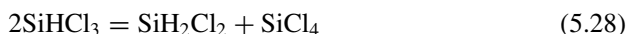
Figure 5.2 Schematic representation of the Siemens process

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 boiling point of other silanes frequently found with trichlorosilane are as follows: SiH_4 (-112°C), SiH_2Cl_2 (8.6°C) and SiCl_4 (57.6°C). 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 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 , growing large rods of hyper-pure silicon.

The main reactions are:



The stream of reaction by-products, which leaves the reactor, contains H_2 , HCl , HSiCl_3 , SiCl_4 and H_2SiCl_2 .

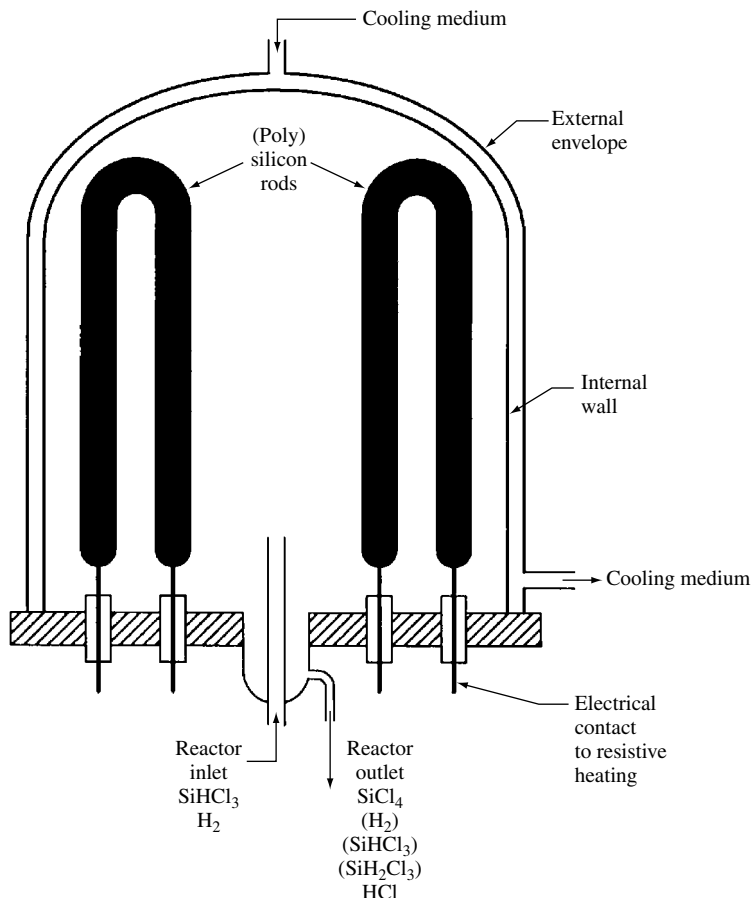


Figure 5.3 Schematic representation of the traditional Siemens reactor

A schematic representation of the Siemens reactor is given in Figure 5.3.

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, this has to be cooled. Originally, the decomposition chamber consisted of a quartz bell jar containing one single inverted U-shaped silicon seed rod. A major advancement in polysilicon production was the utilisation of metal bell jars in place of the quartz bell jars. Quartz bell jars could not be produced in large diameters and were susceptible to breakage. The development of steel bell jars made it possible to accommodate 30 or more inverted U-rods in each reactor. This dramatically increased the productivity while decreasing the energy consumption per kilogram of produced polysilicon.

As reactions and equilibria (5.28) to (5.31) show, the deposition process generates by-products. Unfortunately, for each mole of Si converted to polysilicon, 3 to 4 moles are converted to SiCl_4 , 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

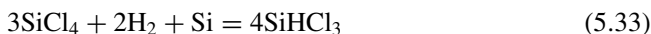
silica is about 60 000 MT measured in terms of silicon unit. This presently corresponds to three times the output of polysilicon in 2000. Moreover, a significant portion of fumed silica is also produced by burning derivated by-products from the silicones industry. In the early stages of the polysilicon 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 today. There are two basic chemical processes applicable to reconvert SiCl_4 to SiHCl_3 :

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



At about 1000°C , a 1:1 molar mixture of SiCl_4 and H_2 produces approximately 20 to 25% molar 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 (5.28) and (5.31).

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



This hydrogenation reaction produces approximately 20% trichlorosilane at 500°C , 35 atm with a 1:1 ratio of SiCl_4 to H_2 in one pass through a mass bed of metallurgical grade silicon in a fluidised 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 ($\sim 230\,000\text{ ohm cm}$) 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 ($\sim 0.1\text{ ohm cm}$). 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 developed processes have attempted to overcome some of these disadvantages.

5.4.2 The Union Carbide Process

Research on this process was initiated in 1976 after the international oil crisis. The US Government funded several projects with the objective of finding a route to inexpensive solar grade polysilicon. The Union Carbide process for silane production, with fluidised bed production of polysilicon, was selected for further funding. When the funding was not provided for political reasons, Union Carbide decided to use the silane technology for the production of semiconductor grade polysilicon. Silane deposition technology for polysilicon rods was licensed from Komatsu Electronic Metals, Japan. In 1990, the business was sold to Komatsu, which became Advanced Silicon Materials (ASiMI). By 1998, two large industrial plants were constructed in the United States with the nominal capacity of 5500 MT polysilicon, thus ranking ASiMI as number two or three worldwide among the polysilicon producers. A schematic overview of the process is given in Figure 5.4.

The main process steps 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 (5.33).

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

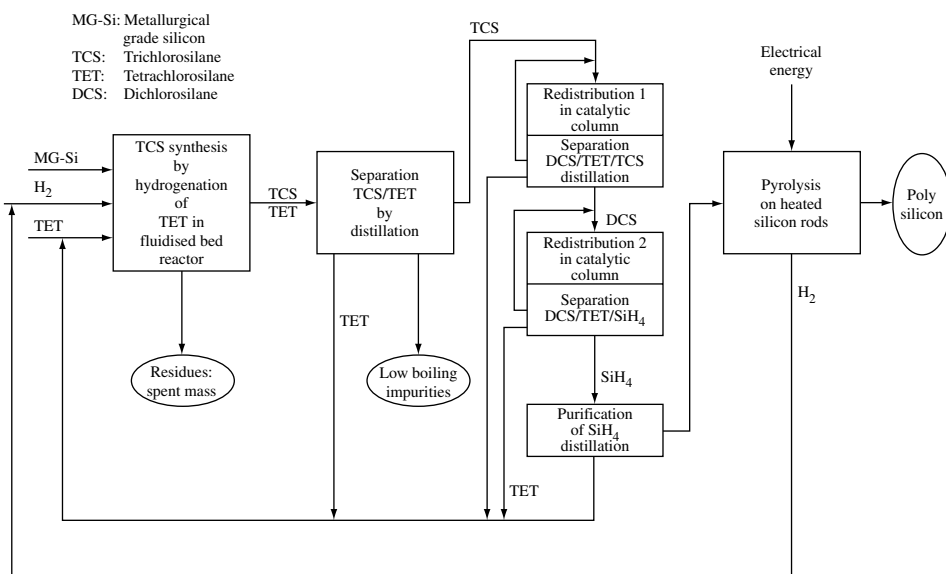
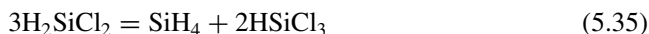
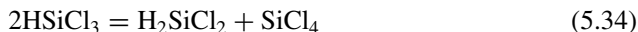


Figure 5.4 A schematic representation of the Union Carbide Polysilicon process

The purified trichlorosilane is then redistributed in two separate steps through fixed bed columns filled with quarternary ammonium ion exchange resins acting as catalyst to both redistribution equations (5.34) and (5.35):



Products of (5.34) and (5.35) are separated by distillation. Tetrachlorosilane and trichlorosilane are recycled to the hydrogenation (5.33) reactor and the first redistribution step (5.34), 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 of metallurgical grade silicon in granular form designed for fluidisation. Because equations (5.33) to (5.35) yield low portions of suitable products and because distillation has to take place after each of them, the intermediates tri- and tetrachlorosilane are recycled and purified many times before conversion to silane. This results in extremely high purity for the silane and the subsequent polysilicon. This is operated as a closed-loop process, not as a batch process.

Other advantages of using 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.

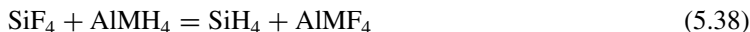
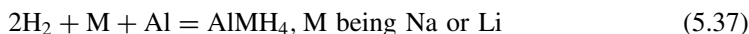
The disadvantage of the monosilane-based process is the higher cost of the volatile molecule, since additional steps are requested to convert trichlorosilane to monosilane. Moreover, the recycling of unsuitable chlorosilanes is compulsory when choosing this option because the redistribution equations yield only a small percentage of the suitable silane.

5.4.3 The Ethyl Corporation Process

This process was developed by the US company Ethyl Corporation at the same time, in similar conditions and political context as the above-described Union Carbide process. Although managed differently, the outcome of both projects was similar in the sense that both shifted their focus from solar grade polysilicon and ended up as new commercial polysilicon processes serving the electronic industry. The Ethyl Corporation process is, by comparison with the Siemens and the Union Carbide processes, revolutionary in all aspects except 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 fertiliser industry. Tens of thousands of tonnes 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.



AlMF_4 is believed to find application in the aluminium industry, making it a valuable saleable product.

After distillation, monosilane SiH_4 is thermally decomposed to polysilicon as described by (5.36). However, to realise 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 5.5.

The fluidised bed reactor offers some 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 operates at a lower temperature and because the same 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.

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).

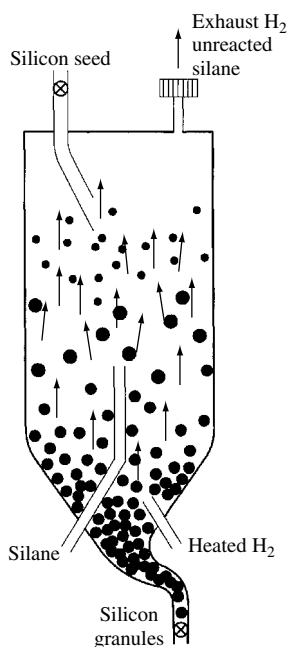


Figure 5.5 A schematic representation of a fluidised bed reactor for polysilicon production

A disadvantage of the process is the generation of powder due to homogeneous decomposition of SiH_4 in the free reactor space and the hydrogen absorption into the polysilicon deposition layer.

5.4.4 Economics and Business

The polysilicon business is completely dedicated to the semiconductor industry and therefore is a high-technology, fast-growing (annual growth approximately 10% on average) and cyclical business. With an average price of 50 US\$ per kg and a sale of 20 000 MT, it is a global business of one billion US\$ supporting a multibillion US\$ semiconductor market. Physical volumes are small but added value is high. This may be judged by taking into consideration that metallurgical grade silicon at 1 US\$ per kg is the only raw material necessary. Small amounts of hydrogen and chlorine or tetrachlorosilane are purchased as make-up to compensate losses occurring in the closed-loop process.

The industry is extremely capital-intensive. Plants have capacities ranging from 1000 to 5000 MT. One unit of 1000 MT may require a capital expenditure of 100 million US\$.

The second characteristic is that the decomposition process requires large amounts of energy. In the early stages of the industry, consumption of 350 kWh per kg polysilicon was not unusual. Efficiencies improved to 150 to 160 kWh per kg, and advanced processes are now about 100 kWh per kg. The fluidised bed process is even more efficient.

The industry is concentrated in the United States (five plants, four producers), the European Union (two plants, two producers) and Japan (three plants, two producers). Small plants are also operating in PR China and the Commonwealth of Independent States (CIS).

Polysilicon is then melted and solidified into a single crystal either by the Czochralski (CZ) or by the floating zone method (FZ). Large single crystal ingots or boules are then sliced into wafers onto which semiconductor devices are built. About 15% of polysilicon production is used to make single- and multicrystalline silicon wafers for solar cell applications.

As it is an important aspect of the PV industry and sciences, crystallisation technologies are covered in Chapter 6 of this handbook and some basic principles are given in the next section of the present chapter.

5.5 CURRENT SILICON FEEDSTOCK TO SOLAR CELLS

Elemental silicon is used in photovoltaics as the main semiconductor material converting light to electricity. Two main classes of silicon must be distinguished: amorphous and crystalline. Crystalline cells are either single- or multicrystalline. Within each group of technology several variants may be distinguished. The elaboration of the cells by different silicon-based technologies and their characteristics are described in Chapter 7. According to recent market surveys [1–3], crystalline silicon is strengthening its dominant position, particularly multicrystalline silicon (including ribbon) with new capacities steadily coming on stream. (See Table 5.3 and References [1–3].)

Table 5.3 Solar modules shipment by technology Source: PV News 2001, Reference [1]

Technology	1998 [MW]	1998 [%]	2000 [MW]	2000 [%]
Single-crystalline silicon wafers	61.5	39.7	89.7	31.2
Multicrystalline silicon wafers	67.0	43.3	140.6	48.9
Ribbon/multicrystalline silicon film	6.0	3.8	16.7	5.8
Amorphous silicon/single-crystalline silicon	—	—	12.0	4.2
Amorphous silicon	19.0	12.3	27.0	9.4
Others	1.4	0.9	1.7	0.6
Total terrestrial PV shipments	154.9	100	287.7	100

(i) *Amorphous silicon*. Monosilane (SiH_4) is the source of silicon required for the deposition of silicon amorphous thin film in a glow discharge or low temperature plasma. Silane is mass-produced by the Union Carbide (ASiMI) and Ethyl Corporation (MEMC) methods, which are described above. The global annual output capacity is approximately 7000 MT including minor volumes produced in Japan. The major part of it is used to produce polysilicon on site (United States), the balance being sold through distributors, for example industrial gas companies, to a vast group of customers. The worldwide silane market for silicon films in the semiconductor, PV, glass and ceramic industries is about 500 MT. Applications include passivating and semiconducting layers for integrated circuits, epitaxial films, architectural glass coatings, special ceramics, surface treatment and amorphous silicon. Silane is available in quantities and purity exceeding the need of the PV market. Quantity and cost of silicon is of less importance for amorphous silicon since the specific consumption per watt output is 50 to 100 times less than that for crystalline silicon cells, that is, 100 to 400 mg/W versus 10 to 20 g/W.

(ii) *Crystalline silicon*. Regardless of the technology, significant quantities of silicon are required to produce multicrystalline silicon solar cells. In the present stage of the technology, 15 to 17 g/W (estimated average value) are consumed. In 2000 this had represented a quantity of approximately 4000 MT. It is expected that this specific consumption per watt will decrease with technology improvement. Firstly, up to 60% of the purchased silicon feedstock is presently wasted during the manufacturing process. Secondly, the thickness of the silicon wafer is unnecessarily high with respect to light conversion. It is presently a mechanical requirement for the further handling of the wafers and the cells. Assuming continuous growth at the same level as during the last decade, several market forecasts predict that the requirement for silicon feedstock will in 2010 reach at least 12 000 MT. If the growth is accelerated as the more recent trends seem to show, the volume demand may be as high as 30 000 MT.

Commercial silicon bulk material is of two types:

- The metallurgical grade, global annual output: 1 million MT, price 0.8 to 1.5 US\$/kg.
- The semiconductor grade, global annual output: 20 000 to 25 000 MT, price 35 to 55 US\$/kg.

Chemical purity of typical metallurgical grade is given in Table 5.2. For some price premium, silicon producers could upgrade it to higher purity by metallurgical treatment

Table 5.4 Metallurgical silicon expected characteristics if upgraded with best currently known metallurgical technology

Impurity	Target concentration [ppm(w)]	Target price [US\$/kg]
Fe	50	5–7
Al	50	
Ca	50	
Ti	5	
C	50	
B	7	7
P	7	
O	200	
Other impurities	Less than 5	

Table 5.5 Specification of chemical impurities in lowest-grade silicon currently purchased to produce multicrystalline silicon wafers

Impurity	Specification
Fe, Al, Ca, Ti, metallic impurities	Less than 0.1 ppm(w) each
C	Less than 4 ppm(w)
O	Less than 5 ppm(w)
B	Less than 0.3 ppm(w)
P	Less than 0.1 ppm(w)

Table 5.6 Electrical specification of lowest-grade silicon currently purchased to produce multicrystalline silicon wafers

Property	Specification
Resistivity	Higher than 1 ohm cm, <i>p</i> -type
Minority-carrier lifetime	Higher than 25 μ s

as tentatively indicated in Table 5.4. However, impurity contents, particularly boron and phosphorus, prevent the use of such material in solar cells. The current minimum purity requested for growing multicrystalline silicon ingots for wafering is given in Tables 5.5 and 5.6.

For semiconductor grade silicon, impurity levels are at least at the ppb level and resistivity within 1000 to 30 000 ohm cm. Although purity requirements for solar cells are not as stringent as for semiconductors, the industry has up to now been forced to select its silicon raw material from the semiconductor silicon source. Silicon is one of the main, if not the largest, cost drivers of the installed PV system. It accounts for approximately 25% of the wafer cost and 15% of the cell cost. Taking into account the dominant share of silicon crystalline technology, the industry is very sensitive to the silicon

price. To reduce price, the industry has therefore selected its silicon raw material from various second-grade classifications of semiconductor silicon, being less expensive than prime-grade polysilicon. We may assume that this feedstock has cost the PV industry, on average, one-third of what prime-grade polysilicon would have cost. The present silicon feedstock for crystalline cells consists of the following factors.

1. *Rejects from crystal growth*: Crystal growth, particularly by the CZ method, generates significant amounts of unusable silicon as follows:

- The head (or top) as well as the bottom (or tail) of the single crystal (also called *ingot* or *boule*). These sections are rejected because of size, defects in the crystalline structure and higher impurity levels.
- Ingots from aborted runs, for example, because of electrical power failure during crystal pulling.
- Ingots or ingot sections that fail to meet the specifications of crystal structure, electrical characteristics or carbon (C) and oxygen (O) content.
- Crucible leavings or pot scrap.

As late as ten years ago, almost half of the polysilicon purchased for crystal growth was rejected for the above reasons. Crystal growth yields have improved and processing techniques have been developed to recycle the higher purity reject material into test or so-called *dummy* wafers. These improvements have reduced the quantity of feedstock available to the PV industry. Rejects from crystal growth, except for the pot scrap, *n*-type, and heavily doped *p*-type material, have been the ideal silicon feedstock for crystalline solar cells. Acceptable quality was available at reasonable prices. We estimate this source at 5 to 6% of all polysilicon shipped, that is, in 2000 approximately 1000 MT. Pot scrap is the remainder of the silicon melt in the quartz crucible after the CZ crystal growth is completed. After solidification, the crucible cracks and pieces of it adhere to the solidified silicon residue. Driven by the need to find new cost-effective sources, the PV industry has found ways to clean mechanically (sand blasting) and chemically (treatment by hydrofluoric acid) selected crucible residues. This has resulted in added quantities to the PV silicon feedstock. We estimated this source at 500 to 700 MT in 2000.

2. *Rejects from polysilicon*: Four to five percent of polysilicon produced is also rejected for quality reasons. These are

- chunks and rods from aborted runs (failure under operation);
- broken or imperfect seed rods;
- “carbon ends,” parts of the rod close to the electrical graphite contacts;
- fines and small chips generated during processing of rods into chunk form;
- “popcorn” or excessive dendritic growth with unacceptable surface texture that may occur under certain operative conditions;
- small granules from the fluidised bed process;
- rod sections that have been sawn or fabricated, so have unacceptable purity.

At 5% of polysilicon produced this amounts to another 1000 MT in 2000.

Rejects from crystal growth and from polysilicon plants in 2000 account in total for 2500 to 3000 MT at most, whereas the consumption has been at least 3500 MT and most probably 4000 MT. The balance has necessarily been covered by standard semiconductor grade polysilicon, either prime grade or a grade produced on purpose for PV customers by some polysilicon producers. As pointed out the present polysilicon capacity exceeds the actual demand by some 5000 MT. It may therefore be attractive for some producers to offer a solar grade in order to optimise their overall costs by operating their plants at higher capacity. This option will be valid for a few years (2–4) as long as installed polysilicon capacity exceeds the semiconductor demand.

Driven by the semiconductor business, polysilicon capacity will not grow as fast as the solar cell market demand. As the semiconductor market matures, the historical growth rates of 15 to 20% appear difficult to sustain; more conservative annual growth rates of 7 to 10% have been projected. Having gone through several high growth/negative growth cycles, the polysilicon producers are now adding capacity only on demand from the semiconductor industry, with guaranteed supply contracts. The producers attempt to avoid large oversupply and inventories, thereby reducing the quantity of polysilicon feedstock available to the PV industry. An annual growth of 20% is predicted as an average or “business as usual” growth rate for the solar market. The polysilicon feedstock shortage for PV can therefore only become worse. The challenge is to develop an alternative source of silicon feedstock competitive in quality and price. The fast-growing solar cell market needs to have a feedstock supply independent of the semiconductor market cycles and growth limitations.

This source must emerge as soon as possible and no later than 2004 to 2005, when polysilicon capacity has been planned to be fully booked again by semiconductor demand. This source should be readily scalable to provide more than 10 000 MT by 2010 at a price less than half the price of semiconductor grade polysilicon.

5.6 REQUIREMENTS OF SILICON FOR CRYSTALLINE SOLAR CELLS

Before exploring the potential routes to solar grade silicon, it is worth looking at the structural and chemical limitations imposed on silicon to reach optimal performances for crystalline and particularly for multicrystalline solar cells. After a short description of the valid principles of crystallisation, we will examine the effect of various impurities and the effect of structural imperfections.

5.6.1 Solidification

When silicon solidifies, a homogeneous melt will normally not result in a homogeneous solid. Concentration gradients will appear as shown in the Figures 5.6 and 5.7.

A schematic phase diagram of the silicon corner is shown in Figure 5.6. When cooling a melt of composition X_0 , it starts to solidify at a temperature T_0 . At a lower temperature, T_1 , a fraction has solidified. At equilibrium the fractional compositions of

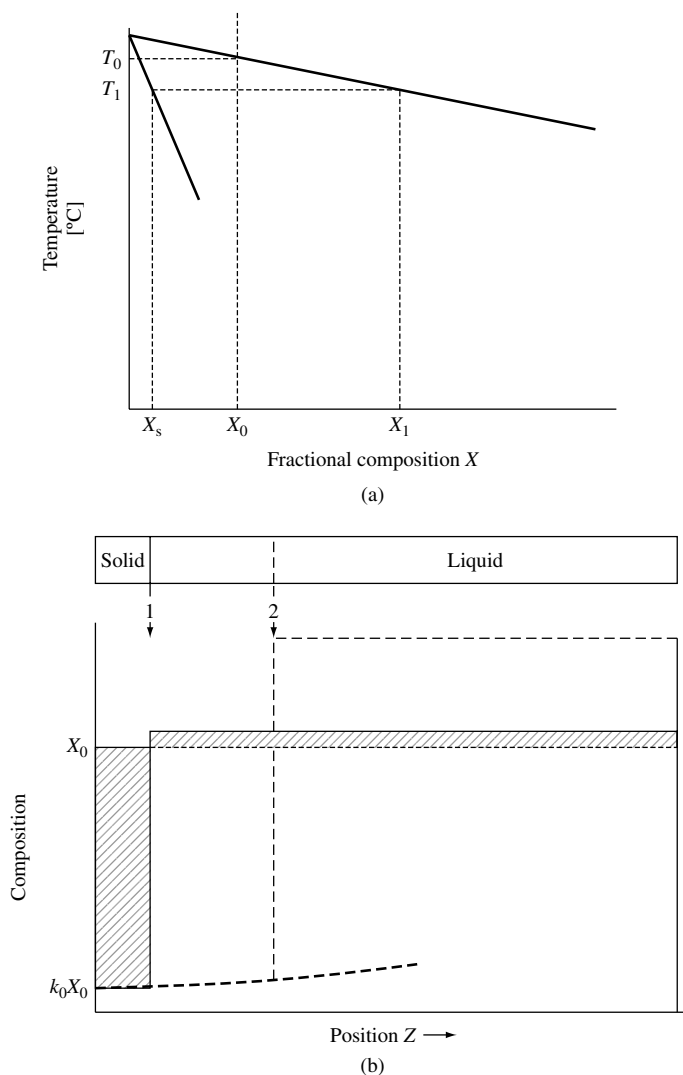


Figure 5.6 (a) Left side of a phase diagram with $k_0 < 1$ and (b) composition development in solid and liquid along a rod solidified from the left end under “normal freezing”

the solid and liquid are X_s and X_1 , respectively. The equilibrium distribution coefficient k_0 at T_1 is defined as the ratio of the equilibrium solid and liquid compositions:

$$k_0 = X_s / X_1$$

(at *equilibrium* both the solid and the liquid have homogeneous compositions X_s and X_1 , respectively).

During normal freezing the solid and the liquid are not in equilibrium. This principle can be used to purify the material. If (1) the solid–liquid interface is flat, (2) the

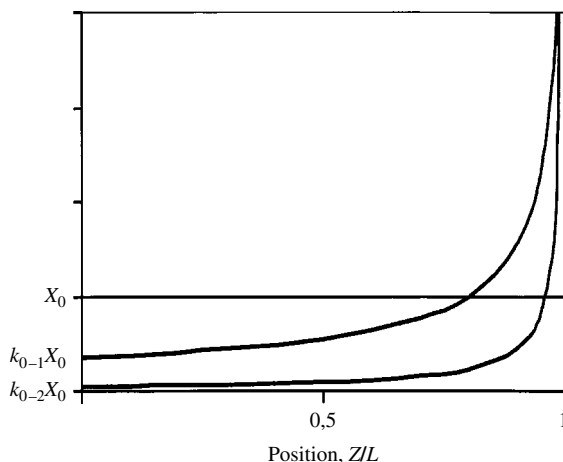


Figure 5.7 Composition profile after the entire rod of Figure 5.6 has solidified, illustrating normal solidification at two different values of k_0 , $k_{0-1} = 0.35$ (upper curve) and $k_{0-2} = 0.05$

melt has a uniform composition and (3) negligible diffusion takes place in the solid, a composition profile like the one in Figure 5.6 is obtained when equilibrium prevails at the interface.

A horizontal cylinder of liquid alloy of initially uniform composition X_0 is cooled at the left end (see Figure 5.6b). Let a small amount of solid form so that the solid–liquid interface is located at position 1. When a small volume has solidified, the composition in that volume has dropped from X_0 to k_0X_0 . A mass of solute proportional to the cross-hatched area to the left of position 1 has been removed from the solid and rejected into the remaining liquid. This will increase the liquid composition to a level above X_0 . If we consider that local equilibrium prevails at the solid–liquid interface during solidification, the liquid and solid compositions at the interface are tied together by the equation $X_s = k_0X_l$. So when the composition of the liquid is raised, the solid composition must also rise as solidification proceeds. When the solid–liquid interface has moved to position 2, the solid composition will have gradually increased, as shown in Figure 5.6(b).

It is shown in Figure 5.7 that k_0 will have a marked effect on the distribution of impurities in solid silicon. Values of k_0 for different elements are given in Table 5.7 [24, 25]. For impurities having a low value of k_0 , for example, $k_{0, \text{Fe}} = 8 \times 10^{-6}$, the solidification process has a large purifying effect: only one Fe atom out of about 100 000 in the melt will enter the solid when solidification starts. For elements in which k_0 is near to 1, no marked change in the concentration of impurities will appear between the melt and the solid silicon.

During the solidification process, the impurity concentration at the interface varies with the fraction of melt solidified and k_0 . If the solute rejected into the boundary region is not transported immediately into the melt in front of the interface, solute will build up at the boundary. As the solute builds up, however, its concentration gradient across the boundary layer becomes steeper and the rate of transport through the boundary layer by diffusion increases until a balance is obtained between the solute being rejected into and

Table 5.7 Distribution coefficients, k_0 , for some elements in silicon at the melting point [24, 25]

Element	k_0	Element	k_0
B	0.8	Ti	3.6×10^{-4}
Al	0.002	Cr	1.1×10^{-5}
Ga	0.008	Mn	1×10^{-5}
N	7×10^{-4}	Fe	8×10^{-6}
P	0.35	Co	8×10^{-6}
As	0.3	Ni	8×10^{-6}
C	0.07	Cu	4×10^{-4}
O	0.25–1.25	Zn	1×10^{-5}

out of the boundary layer. At this point the ratio $(X_1)_{\text{interface}}/(X_1)_{\text{bulk}}$ becomes constant. The effective distribution function k_{eff} is defined as

$$k_{\text{eff}} = X_{\text{s, interface}}/X_{\text{l, bulk}}$$

and tells a great deal about liquid mixing in front of the interface. Poor mixing in the melt results in $k_{\text{eff}} = 1$. Good mixing (no build-up) means $k_{\text{eff}} = k_0$.

Burton *et al.* [26] have derived an expression for k_{eff} when a rotating crystal is pulled from the melt at a velocity v :

$$k_{\text{eff}} = k_0/[k_0 + (1 - k_0)\exp^{-\Delta}]$$

where

$$\Delta = v\delta/D_1 \text{ and } \delta = 1.6 D_1^{1/3} \cdot v^{1/6} \omega^{-1/2}$$

where δ is the distance from the growing interface to where the concentration in the melt is uniformly equal to $X_{\text{l, bulk}}$, D_1 is the diffusion coefficient of the solute, v is the viscosity and ω the crystal rotation rate.

Kodera [27] has applied this to obtain δ/D_1 and D_1 values for melts doped with various impurities at different rotating rates, as shown in Table 5.8. For CZ-grown silicon where v is around 1 mm/min, Δ is small and k_{eff} is close to k_0 [24].

The ability to purify molten feedstock by solidification will therefore vary for the different impurities and with solidification velocity. The validity of the assumption of no diffusion in the solid will not be met at a slow solidification rate and some “back” diffusion will take place. In addition, impurities diffuse from the crucible into the solid, the rate depending on temperature and time. Selection of the optimal casting process parameters is complicated and improvements will depend on the ability to model the total solidification process.

5.6.2 Effect of Crystal Imperfections

Silicon has a diamond lattice atomic structure being cubic with atoms joined to four nearest neighbours by covalent bonds at tetrahedral angles. If the atoms are represented

Table 5.8 Values of δ/D_1 and D_1 for some elements [27]

Impurity element	Rotation rate [rpm]	$\frac{\delta}{D_1}$ [s/cm]	Diffusion coefficient, D_1 [cm ² /s]
B	10	170 ± 19	$(2.4 \pm 0.7) \times 10^{-4}$
	60	84 ± 37	$(2.4 \pm 0.7) \times 10^{-4}$
Al	10	86 ± 34	$(7.0 \pm 3.1) \times 10^{-4}$
	60	40 ± 17	$(7.0 \pm 3.1) \times 10^{-4}$
P	5	127 ± 36	$(5.1 \pm 1.7) \times 10^{-4}$
	55	60 ± 19	$(5.1 \pm 1.7) \times 10^{-4}$
As	5	190 ± 53	$(3.3 \pm 0.9) \times 10^{-4}$
	55	79 ± 16	$(3.3 \pm 0.9) \times 10^{-4}$

as hard spheres, the diamond structure fills 0.34 of the available space, compared to 0.74 for a close-packed structure such as aluminium. The formation of defects in the silicon lattice creates local electronic disturbances because of the nature of the atomic bonding.

The following description follows standard textbook presentations in physical metallurgy and concentrates on some lattice defects appearing in silicon, which are important when discussing the effect of impurities on the electronic properties.

It is common practice to divide the lattice defects into the following categories:

Plane defects

Stacking faults

Twin boundaries

Grain boundaries

Line defects

Dislocations

Point defects

Vacancies

Self-interstitials

Substitutional impurities

Interstitial impurities

Volume defects

Precipitates

Single-crystal material consists of one grain of a continuous crystal structure. Multicrystalline (mc-)/polycrystalline (pc-) material consists of many separate grains with inclined crystal planes that meet at *grain boundaries*. Depending upon the misorientation between adjoining grains, the interfaces are termed *subgrain* boundaries ($0-5^\circ$) and *grain* boundaries. *Twin* boundaries arise where one crystal grain is a mirror image of its neighbour. Grain boundaries may have a more open and less well organised atomic structure. Atomic diffusion is therefore easier along grain boundaries than in the bulk crystal. Because of the lack of crystal order, some of the covalent bonds are broken and the grain boundaries may therefore carry electric charge. The electrical properties of the grain boundaries vary with the amount of atomic disregister.

The concept of a linear lattice imperfection called a *dislocation* arose primarily from the study of plastic deformation of crystalline materials. The dislocations are borderlines where the atomic planes are out of register. At dislocations some of the covalent bonds in silicon are broken. The dislocations may therefore carry electric charge.

Because of the disregister, the dislocations are surrounded by stress fields and may attract impurity atoms.

In *n*-type silicon, donor impurities can provide electrons to fill the missing charge from a missing bond at the dislocation. As a result of the acquisition of electrons, the dislocation becomes negatively charged, which again may attract the positively charged donor impurities. This situation may lead to a space charge region in the form of a cylinder in which positively charged donor ions surround a negatively charged dislocation.

In *p*-type material, the dopant atoms may accept electrons from a dislocation. In this case the cylinder-shaped space charge region has a positively charged dislocation surrounded by negatively charged acceptor ions.

The category of *point defects* include vacancies, interstitials and impurities either present as intentionally dopant atoms added to control the properties of silicon or unintentionally incorporated as contaminants from the raw materials, processing or crystal growth.

A *vacancy* is a missing atom at a silicon site. The result of the removal of a silicon atom is the formation of four dangling atomic bonds with unpaired electrons and some lattice relaxation. Vacancies thus tend to exhibit acceptor-like behaviour. The concentration of vacancies, n/N_0 , in silicon at a given temperature can be determined from the following expression:

$$n = N_0 \exp(-E_v/kT)$$

where n = number of vacancies/volume, N_0 = number of atoms/volume, k = Boltzmann's constant and T = temperature in K. E_v is the formation energy, which is the energy required to take an atom from a lattice site inside the crystal to a lattice site on the surface. In silicon, $E_v \approx 2.3$ eV.

A *self-interstitial* can be formed by inserting a silicon atom into one of the holes in the structure. The energy of formation of interstitials, E_i , in the loosely packed diamond structure is lower than the formation energy of vacancies, $E_i \approx 1.1$ eV.

An interstitial has four valence electrons that are not involved in covalent bonding with the adjoining atoms. These electrons may be lost to the conduction band and the interstitial may behave as a donor.

At low concentrations the impurities exist as single atoms in the matrix – so-called *solid solutions*. Atoms in the solid solution are incorporated in the matrix in two ways. They can substitute for an atom of the host crystal and maintain the regular atomic structure of the crystal. In this case they are known as *substitutional impurities*. Alternatively, the impurity atoms can occupy positions squeezed in between the atoms of the host crystal. Then they are known as *interstitial impurities*.

The energy levels associated with point defects in silicon are fairly deep. They serve as centres for minority-carrier recombination and therefore reduce the carrier lifetime. The lifetime is inversely proportional to the concentration of point defects.

The diffusion of atoms in a crystal proceeds by thermally activated jumps from sites to sites. The diffusivity is expressed by the diffusion coefficient, D , with units cm^2/s :

$$D = D_0 \exp(-E_D/kT)$$

where D_0 is a constant and E_D is the activation energy for the jumping process.

At higher concentrations the impurities may agglomerate. The ability to be in solid solution increases with temperature (see Section 5.6.3). The impurities in a material at a certain purity level may thus be in solid solution at elevated temperatures and form *pairs* with other atoms or *precipitate* at dislocations, at grain boundaries or with other impurities at lower temperatures. The sequence of precipitation is characterised by *nucleation*, *growth* in which excess atoms diffuse to precipitates and *Ostwald ripening* in which a growth competition exists where large precipitates grow at the expense of small ones.

Minority carriers (being electrons on the *p*-side and holes on the *n*-side of the solar cells) flow more readily within a grain than across grain boundaries. Minority carriers may recombine with majority carriers at recombination centres like impurities, precipitates, dislocations and grain boundaries. The average distance that a minority carrier will travel within silicon depends upon the density of recombination centres and their recombination ability. The longer the distance between recombination centres, the better the efficiency of the cell. Precipitation of impurities reduces the number of atoms in solid solution and may therefore change the minority-carrier diffusion length. The density of precipitates is governed by the cooling rate, the ramping sequences and the diffusivity of the impurity elements.

At the surface there are many recombination sites. In the final cell production sequence, gettering and passivation will change the conditions near/at the surface.

Measurements of the local electronic properties in individual grains and near grain boundaries show that the properties may vary from grain to grain. It is hoped that the results of such measurements may stimulate further theoretical and experimental work to clarify the relations between grain structure and the electronic properties in multicrystalline silicon.

The density of dislocations influences the lifetime of the minority carriers. Experiments show good correlation between areas having a high dislocation density and a short effective lifetime. To control the dislocation density has therefore become an important task. The dislocation movements and multiplication and their interaction with impurity atoms being in solid solution or existing as complexes during the production processing steps challenges our ability to model complex relationships. However, it is being claimed that numerical simulation is used as a valuable tool to optimise the crystallisation and cooling processes at plants. This is the kind of work that certainly will develop during the coming years.

5.6.3 Effect of Various Impurities

It is well known that impurity atoms have a strong effect on the efficiency of silicon as a photovoltaic material. It is also known that the effect of impurities can be changed by heat treatments and by exposing the material to gettering atmospheres in which selected elements diffuse into silicon and combine with the impurities (a semantic parallel to getter pumps in which oxygen is adsorbed by certain elements).

The impurity atoms may appear as solid solutions, as pairs with other elements, for example FeB, or as larger aggregates/precipitates with silicon and/or other elements, for example Fe₂Si. This depends upon the temperature, the concentration and the density of the imperfections (dislocations, grain boundaries). If the temperature or the (chemical) surroundings are altered, it will take some time before a new equilibrium is established. The time to reach equilibrium may depend on parameters such as temperature, cooling/heating rate, and chemical composition, grain size, dislocation density and others. When comparing results from literature values in which the specifications of relevant parameters are not defined, it is likely that differences may appear.

Most of the impurities in silicon used for PV cells exist at very low concentrations. Since measurements of trace quantities are difficult, much of the progress has occurred when new and better instrumentation has become available. Over the years many review articles and books dealing with the effect of impurities in crystalline silicon have been published. The interested reader is therefore encouraged to look up some of the references for a wider treatment of the subject [25, 28–33]. The following will therefore be an attempt to briefly summarise and update the general knowledge of the subject.

The maximum solid solubilities, $X_s(\text{max})$, of impurities in silicon are related to the distribution coefficients at the melting point according to an empirical relation found by Fischler [34]:

$$X_s(\text{max}) = 0.1k_0$$

or in units of atoms/cm³:

$$C(\text{max}) = 5.2 \times 10^{21} k_0$$

Although deviations have been found for nitrogen, carbon and oxygen [35], the relation may be useful.

5.6.3.1 Atoms from Groups IIIA (B, Al, Ga...) or VA (N, P, As, Sb...)

These atoms act as substitutional impurities in silicon. At a site where a Group VA impurity (e.g. phosphorus) has replaced a silicon atom, four *d*-electrons are bound to the Si neighbours, while the fifth electron is weakly tied to the Group VA atom. The fifth electron is not completely free to move, but it is easily activated to the conduction band. Group VA atoms are therefore *donor* atoms.

In an analogous way, Group IIIA atoms (e.g. boron) do not have enough valence electrons to satisfy the four covalent neighbour bonds. This gives rise to holes weakly tied to the Group IIIA atoms. These impurities therefore create energy levels for electrons in the forbidden gap just above the valence band edge. Group IIIA atoms are called *acceptors*.

To be able to control the level of doping, the concentration of unwanted elements from the Groups IIIA and VA must be well below the concentration of the doping element.

Our theoretical understanding of the properties of impurities in silicon other than those from the Groups IIIA and VA is less well developed. However, as new instrumentation has become available, a lot of experimental results of high scientific standard have been published.

5.6.3.2 Carbon

Carbon is a common substitutional impurity. Like silicon it has four valence electrons and is therefore electrically neutral. The carbon atom is smaller than the silicon atom and may therefore be involved in precipitation of species expanding the lattice like silicon oxide.

The solid solubility limit is $C_S = 3.5 \times 10^{17}$ atom/cm³ at the melting point or $C_S(T) = 4 \times 10^{24} \exp(-2.3 \text{ eV}/kT)$ atoms/cm³, where k is the Boltzmann's constant [89, 91].

In metallurgical grade (MG) silicon, carbon is present at levels above the solid solubility limit and SiC precipitates are commonly present. In electronic grade (EG) the concentration of carbon is low. But in contact with the crucible and the carbon-rich atmosphere (graphite), it is difficult to avoid contamination of the melt.

As a substitutional element, carbon diffuses rather fast [$D = 1.9 \exp(-3 \text{ eV}/kT)$ cm²/s], but much slower than interstitial impurities.

5.6.3.3 Oxygen

The subject of oxygen atoms in silicon has been studied for many years. Since results from experiments performed under different thermal histories have varied, the discussion goes on.

Oxygen atoms in solid solution are electrically inactive and predominantly enter interstitial sites. The equilibrium value of the solid solubility at the melting point is generally accepted to be 1×10^{18} atom/cm³. However, the results from measurements of solid solubility as a function of temperature differ markedly. The value of k_0 will therefore vary (see Table 5.7).

In a work by Itoh and Nozaki [32] an important point was made that the concentration of oxygen at equilibrium at a given temperature was determined by the type of oxide that was stable at that temperature. So if the type of oxide varied, it would be expected that bends in solid solubility curves at temperatures at which the silicon oxides change would be observed. However, up to 1200°C, SiO₂ is the stable chemical form and the solubility $L = \exp(\Delta S/R) \exp(-\Delta H/kT)$ will have constant values of ΔS and ΔH .

On cooling, super saturation is easily obtained and oxygen precipitates at a rate that depends on oxygen content, temperature, and time at temperature and nucleation sites. Carbon is also found to influence the precipitation of silicon oxides, possibly because the carbon atoms reduce the expansion of the lattice when silicon oxide is growing.

Oxygen has a high diffusion coefficient, $D = 0.13 \exp(-2.53/kT)$ [36]. By heat treatments, the distribution of oxide particles may change since particles may get dissolved when heated and grow when cooled. Oxygen atoms are found to change the effect of other impurities, a process known as internal gettering.

One important oxygen source is the crucible. Silicon is normally melted in high-purity-fused quartz (SiO_2) crucibles (single crystals) or quartz crucibles coated with high-purity Si_3N_4 (multicrystalline ingots). If holes appear in the coating, quartz will easily dissolve in the melt and raise the level of oxygen in the solid.

The variety of effects observed with oxygen in silicon will truly stimulate further research for a long time.

5.6.3.4 Transition metals

Properties of transition-metal impurities in silicon have been reported in a large number of articles, reviews and books [28–30, 33]. The transition metals are presented by the symbols 3d, 4d and 5d, which specify the outer electron configuration of a neutral atom. Most of the metals forming deep energy levels (“midway” between the conduction band and the valence band) in silicon belong to this group and have therefore a large influence on the electronic properties of silicon.

The main impurities found in silicon belong to the 3d transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu). In general, these are present as interstitial impurities.

The diffusivity increases with increasing atomic number in the 3d row (see Figure 5.8), with Ni and Cu having the largest diffusion coefficients known in silicon.

The concentration of vacancies is very low in silicon. The high diffusion coefficients of 3d elements can therefore only be explained by interstitial diffusion mechanisms independent of vacancies.

The 3d transition metals have a steep temperature-dependent solid solution limit that make them easily supersaturated during cooling (see Figures 5.9 and 5.10). They therefore frequently form complexes/precipitates at dislocations, grain boundaries or other lattice defects.

The solubility at room temperature is very low, of the order of 1 atom/cm^3 . However, some 3d impurities are mobile even at room temperature. So the atoms with the highest mobility (Co, Ni, Cu) will be out of the solid solution during or just after the cooling. The 3d metal atoms with a low diffusivity may remain in the solid solution at interstitial sites for a much longer time after cooling. This may depend upon crystal perfection, which determines the diffusion length to reach sinks such as dislocations, grain boundaries and precipitates.

The solid solubility of the 3d transition metals in silicon is shown in Figure 5.10.

A severe deterioration of the electrical properties is expected from solid solution impurities capturing the minority carriers (being electrons on the p -side of a p - n

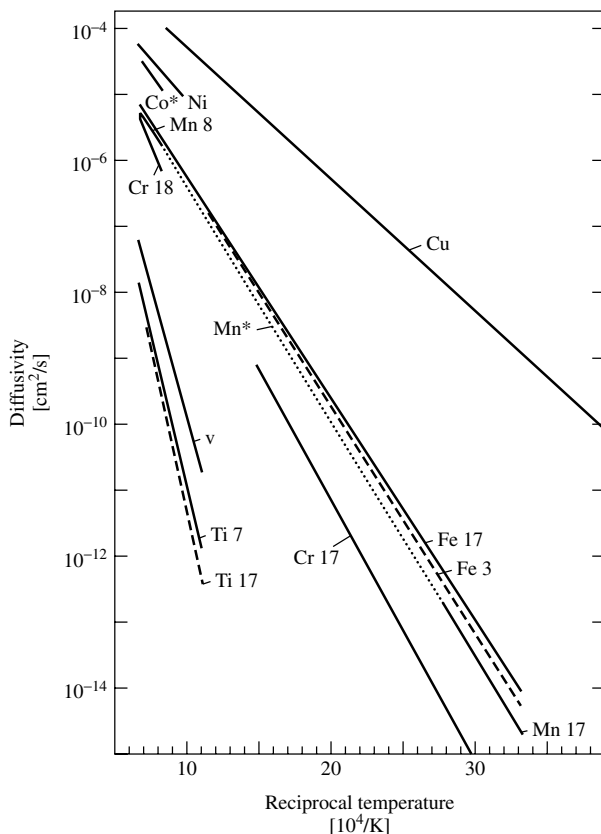


Figure 5.8 Diffusivities of 3d transition elements. Reproduced from *Metal Impurities in Silicon-Device Fabrication*, Graff K, 29, 2000, © Springer-Verlag GmbH & Co. KG

junction). The low-injection-level minority-carriers lifetime, τ_0 , is inversely proportional to the impurity concentration, $N(1/\text{cm}^3)$ [28]:

$$\tau_0 = (\sigma v N)^{-1}$$

where v is the thermal velocity, which is the average speed of the electrons as they randomly collide with atoms, impurities or other defects, and σ , having the units of cm^2 , represents the impurity atoms effective cross-section for the capture of a minority carrier.

Here the carrier capture cross-section for electrons, σ_e (cm^2), must be inserted for p -type silicon and σ_h for holes in n -type silicon. The thermal diffusion velocity v of electrons at room temperature is 2×10^7 cm/s.

The capture cross-sections for different transition metals can differ by several orders of magnitude. As a consequence, the carrier lifetime of a silicon sample can even be determined by an impurity of minor concentration if this is a “lifetime killer” with a high

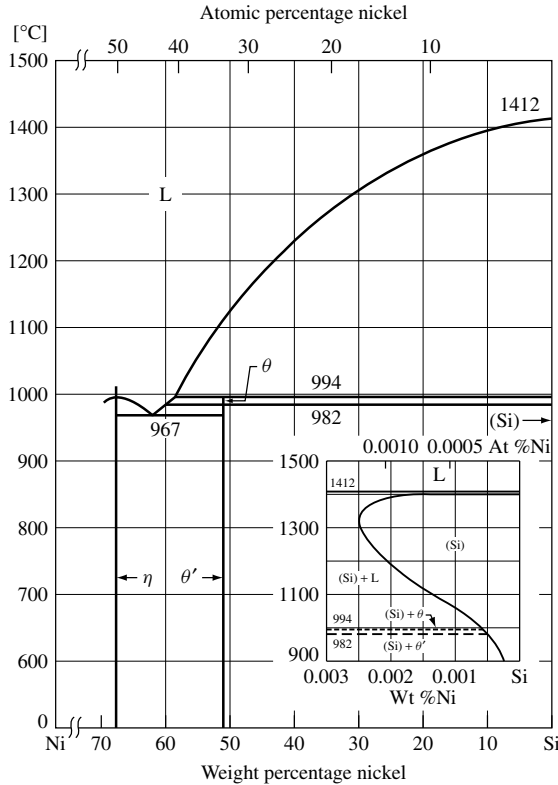


Figure 5.9 The Ni-Si phase diagram. The shape of the solidus line on the Si side is shown in the inserted window. It is seen that the solid solubility of Ni in Si is low, that it increases at temperatures above the peritectic point (at 994°C) (retrograde solubility) and reaches a maximum at about 1300°C. Redrawn from ASM Handbook, Vol. 8, *Metallography, Structures and Phase Diagrams* 8th Edition, ASM International, Materials Park, Ni-Si Phase Diagram, p. 325

minority-carrier capture cross-section. Therefore, the tolerable impurity concentration for acceptable lifetime values depends upon the chemical nature of the respective impurity, and its carrier capture cross-section for electrons in *p*-type silicon and for holes in *n*-type silicon. Both parameters can differ by orders of magnitude and consequently the acceptable concentration for a defined impurity can be quite different in *p*- and *n*-type silicon (Figures 5.11 and 5.12; [30]).

Copper and nickel have high diffusivities and low capture cross-sections. These elements will rapidly enter a low solid solution level after cooling to room temperature and may therefore be expected to have less effect on lifetime than elements with lower diffusivities (Fe, Ti) and high capture cross-sections.

5.6.3.5 Precipitates

Except for copper, which forms Cu_3Si particles when cooled, the other 3d metals form MeSi_2 precipitates. Investigations of crystallographic structure, morphology and

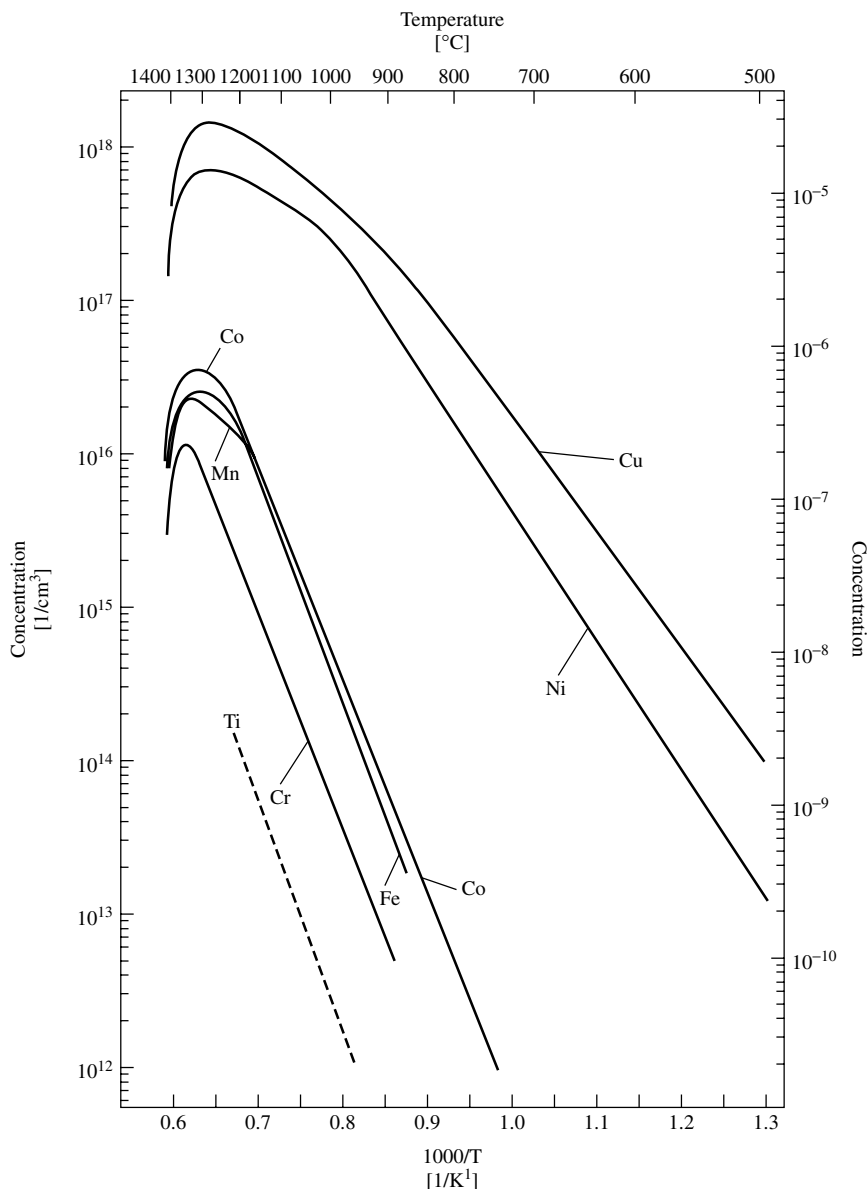


Figure 5.10 Solid solubility of 3d transition elements in silicon. Sc is still missing, but is assumed to be a little below the values of Ti. Adapted from *J. Appl. Phys.* Weber E, **A30**, 1–22 1983, © Springer-Verlag GmbH & Co. KG. The values for Ti are taken from [37]

composition of several transition-metal precipitates in silicon identify crystalline silicides, FeSi_2 , CoSi_2 , NiSi_2 , as compounds that influence the minority-carrier diffusion length. The morphology and density depend upon temperature and time at temperature. Elements having a high diffusivity like Ni and Cu precipitate easily. This reduces the number of atoms in solid solution and may therefore change the electric properties. Kittler and

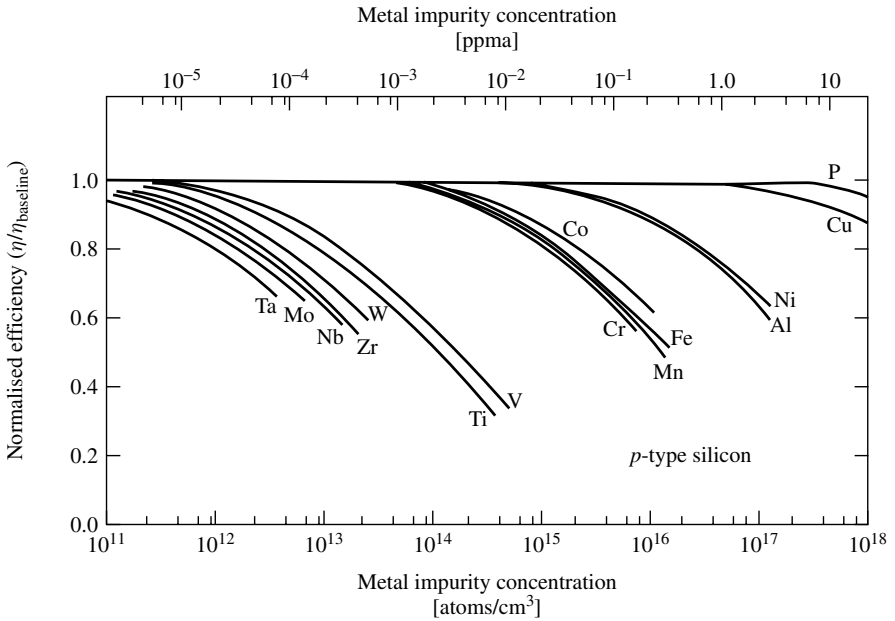


Figure 5.11 Solar cell efficiency versus impurity concentration for 4 ohm cm p-base devices [30]. Reproduced from Davis Jr. J *et al.*, *IEEE Trans. Electron Devices* © 1980 IEEE

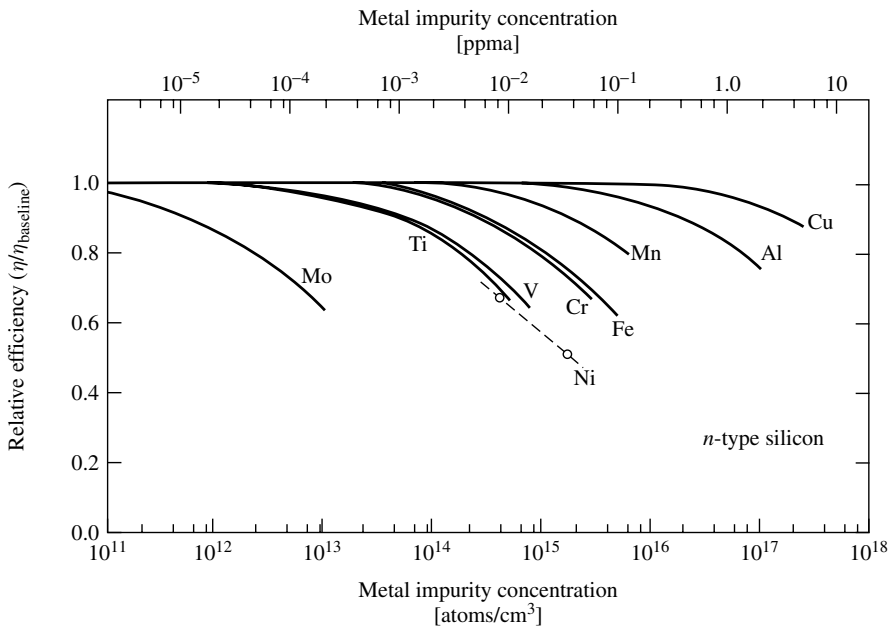


Figure 5.12 Solar cell efficiency versus impurity concentration for 1.5 ohm cm n-base devices [30]. Reproduced from Davis Jr. J *et al.*, *IEEE Trans. Electron Devices* © 1980 IEEE

co-workers [31] studied the precipitation and coarsening of NiSi_2 and the effect of precipitates upon the minority-carrier diffusion length in n -Si single crystals (FZ material). Scanning electron microscopy (SEM) using the method of electron beam-induced current (EBIC) revealed that NiSi_2 precipitates were efficient recombination centres and that the minority-carrier diffusion length, L_D , was related to the precipitate density, N_p , by

$$L_D = 0.7 \cdot N_p^{-1/3}$$

This relationship revealed that the diffusion length depends only on the density of precipitates and not on the concentration of impurities. Therefore, a suitable temperature process can increase the diffusion length, L_D . This occurs if during this process large precipitates grow at the expense of the smaller ones, increasing the free distance between the precipitates. This ripening process of precipitates is observed repeatedly during heat treatments.

5.7 ROUTES TO SOLAR GRADE SILICON

To design a specific route to solar grade silicon between the two existing commercial grades, that is, metallurgical and semiconductor (polysilicon), is not a new challenge. It was first seriously and massively addressed in the mid-seventies after the first international oil crisis. Considerable R&D efforts were made in the years 1975 to 1985 particularly in the United States under the guidance of the Department of Energy (DoE). During and at the end of this productive period, numerous specific articles, exhaustive review-studies and symposium proceedings devoted to these topics were published [38–40]. The following gives a summary and an update of these efforts. All approaches investigated are classified within four subgroups.

1. Crystallisation is generally an effective purification technique. Crystallisation is also a necessary step to produce the silicon device. The question is whether the crystallisation steps in the manufacturing chain to the solar cell can advantageously be combined with the purification.
2. Upgrading the purity of metallurgical silicon is a technique with the potential to produce millions of tonnes of silicon as we have demonstrated earlier in this chapter. The goal of and the challenge for this alternative are to achieve adequate purity at acceptable cost. A guiding number for this option has been and should remain less than 10 US\$/kg.
3. The polysilicon process involving the synthesis, the purification and the decomposition to elemental silicon of volatile silicon hydrides is proven technology. This is presently the sole reliable source of silicon for solar cells. Simplifying it, exploring or revisiting related routes seems therefore an attractive alternative. The challenge in this particular case is to achieve sufficient output at acceptable cost.
4. Electrolysis, electrolytic methods, metallic reduction of silicon and so on are summarised in a fourth category of methods.

5.7.1 Crystallisation

The efficiency of the crystallisation processes may be predicted by the segregation or the distribution coefficient of each impurity element (see Section 5.6.1) between the solid and

the liquid silicon phases. Published data (see Table 5.7) clearly show that the elements belonging to the Group IIIA (B, Al, Ga) and the Group VA (P, As, Sb) have a coefficient close to 1, making it difficult to separate them from the silicon. These elements are the electronic dopants for silicon and their concentration must be closely controlled during all steps of the manufacturing process. Their chemical and physical behaviour in interaction with silicon are two aspects of their close neighbourhood to this element. Crystallisation as such cannot be satisfactory without prior treatments, specifically to remove these elements, particularly P and B.

- *Crystallisation from a silicon-melt*: Various methods have been claimed to be useful for refining silicon by directional solidification resulting in large oriented crystals. All these various crystallisation methods are also used in manufacturing the silicon photovoltaic devices, and they are described in Chapter 6 of this handbook. Other valuable references are to be found in [39, 40].
- *Crystallisation from an aluminium melt*: Silicon forms a unique eutectic phase at the concentration of 12.6%(w) in aluminium. Several companies (Union Carbide, Alcoa and Wacker) have tried to take advantage of this property in order to purify silicon. By cooling a hypereutectic composition, pure silicon phases crystallise and precipitate from the aluminium melt. After solidification of the hypereutectic alloy, the aluminium matrix can be dissolved by leaching, releasing the pure silicon crystals [39, 41–44]. Published data indicated that the aluminium content in the resulting silicon was as high as 300 ppm(w). The segregation coefficient of aluminium in silicon limits further separation. A further reduction of aluminium, by directional solidification of the silicon thus obtained, would add unacceptable cost just for this element. Other metallurgical routes to eliminate Al at 1 ppm(w) level or less need to go through silicon melting and subsequent extraction with the double risk of recontamination and heavy material losses.

5.7.2 Upgrading Purity of the Metallurgical Silicon Route

The processes used in the elaboration of metallurgical grade silicon for the aluminium and the chemical industries proves that most of the metallic impurities could by repetition and combination of methods be decreased to a rather low level, for example 100 ppm(w) (see Table 5.9). Since metals could be further decreased by a post-directional solidification, it was rational to explore the full potential of this expected low-cost route.

5.7.2.1 Use of pure raw materials and pure lining

The use of pure linings in the furnaces and the intermediate vessels containing the liquid silicon was a first approach. It was investigated by several companies and research

Table 5.9 Typical best results achieved with the carbothermic reduction using high-purity raw materials

Impurity	B	P	Al	Fe	Ti
Minimum content ppm(w)	2	1	100	100	10
Maximum content ppm(w)	4	3	300	200	20

consortiums such as Dow-Corning, Elkem/Exxon, Siemens, NEDO, to mention the most accomplished [45–52]. Quartz or silica sand selected for their original purity were chemically treated by leaching or precipitated from water glass solutions. Purified carbon black was used as the reduction material in most of these approaches. The morphology of sand or precipitated silica and carbon black are quite different from, respectively, lumpy crystalline quartz and bulk carbon, charcoal or woodchips currently used in the carbothermic reduction. New technologies, in particular, to agglomerate the powder-like raw materials had to be developed. Pellets consolidated by means of organic non-contaminating binders (e.g. sucrose) or rice hulls perceived as potential high-volume, low-cost raw materials since they contained both silica and carbon are worth mentioning. Extruded pellets of cocked rice hulls, with sucrose, as a binder appeared to be reactive in the submerged arc furnace technology. Using these special raw materials, boron and phosphorus were found in the range of 1 to 4 ppm(w). In standard metallurgical grade, B and P range between 7 and 50 ppm(w), typical average values being around 25 ppm. The boron level achieved with rice hulls could be as low as 1 ppm(w). However, phosphorus was as high as 40 ppm(w) and would request an additional and specific treatment to make use of this source of silicon in solar cells.

5.7.2.2 *Post-treatment by chemical leaching*

Metallic impurities segregate at the grain boundaries, forming intermetallic phases with silicon, basically made of silicides and silicates. Hydrometallurgical upgrading of silicon by acid treatment and leaching has a long history. The *Silgrain* © process, a trademark of Elkem ASA, is currently producing 30 000 MT metallurgical grade silicon by refining ferrosilicon (90% Si) in an acid liquor of ferric chloride. The process is particularly efficient in removing iron and transition elements because these have very low segregation coefficients in silicon. The dissolution of iron and the transition elements in the leaching liquor is eased and enhanced by the formation of stable intermetallic phases with Al, Ca or isostructural elements, for example, Sr, Ba, Ga or a lanthanide. The process has been further developed during the past 15 to 20 years with solar grade silicon as an objective [53–56].

Surface treatment or leaching by hydrofluoric acid or by HCl/HF mixtures is also well known to wash out residual impurities present as oxides and silicates. Grinding silicon prior to leaching to increase the surface exposure is a way to enhance the purification [57, 58]. Acid leaching has therefore been envisaged by several groups and companies, for example Wacker and Elkem, as a post-treatment purification after the carbothermic reduction [53–58].

However, it must be emphasised that this method cannot in practice refine silicon below the dissolution limit characteristic of each element at the solidification composition. For the major impurities Fe, Ca and Al present in metallurgical grade silicon the limit of dissolution as obtained from classical refining in a ladle exceeds by far the ppm level. Effective post-treatment leaching of metallurgical grade silicon has made it possible to achieve less than 10 ppm(w) for these major elements and less than 1 ppm(w) for minor transition elements. One pass of directional solidification was then envisaged as sufficient to achieve the requested purity for solar cells.

The acid treatment or leaching methods is 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, proves that P could be reduced by a factor of 5 down to a concentration less than 5 ppm(w), probably because P is dissolved in calciumsilicide [55, 56]. Adding barium also proves some effect on boron dissolution.

5.7.2.3 Post-treatment by extraction metallurgy in ladle

Post-treatments of liquid silicon are common practices in refining metallurgical grade silicon for applications in aluminium and chemical industry. The objective is then to adjust Al, Ca and possibly C to a suitable concentration of some hundreds or thousands of ppm(w). To that respect the reader may with great benefit consult Schei's *et al.* comprehensive handbook [13, 23]. As described above, crystallisation and leaching are efficient means of removing chemical elements with high ability to segregate from liquid to solid silicon, that is, Fe, and most of the metallic transition elements. Extraction metallurgy from a liquid phase of silicon, either liquid–liquid, liquid–solid or liquid–gas, has received considerable attention in order to remove the critical elements P, B and C. When silicon is kept liquid, it is possible to displace the equilibrium between both phases present and gradually remove the unsuitable impurity, by continuously extracting it.

Impurity(liquid silicon) = Impurity(liquid slag)	<i>K_{sl}/l_s</i>
Impurity(liquid silicon) = Impurity(solid slag)	<i>K_{sl}/s_s</i>
Impurity(liquid silicon) = Impurity(gas)	<i>K_{sl}/g</i>

Particular attention has been paid to boron and phosphorus because these elements are the major *p*- and *n*-type dopants of silicon and because they coexist in metallurgical grade silicon in concentration of one or two orders of magnitude too high for solar cell applications.

Boron has nearly the same affinity towards oxygen as silicon. Boron forms gaseous suboxides BO being analogous to SiO, and its stable oxide B₂O₃ behaves similar to SiO₂ in the presence of alkaline earths at slag-forming temperatures. Therefore, there are good reasons to expect the removal of boron as an oxide constituent of the extracting slag or as a gaseous suboxide at elevated temperature. Both theoretical possibilities have been experimentally verified.

Since the work published by Theuerer in 1956 [59], it has been known that liquid silicon becomes purified with respect to boron when brought in contact with a gas mixture of Ar–H₂–H₂O. The sole role of H₂ and H₂O assisting the extraction has been emphasised by several authors such as Khattak *et al.* [60–63], whereas Amouroux, Morvan *et al.* of the University of Paris [64–67] and the Japanese group of Kawasaki Steel/NEDO [68–72] have underlined the benefit of using an oxidative plasma in the presence of moisture and hydrogen. Amouroux, Morvan *et al.* have also shown that boron elimination was enhanced when fluoride, for instance in form of CaF₂, was injected into the plasma gas.

Experiments in removing B by slag extraction have been done by several companies and groups including Kema Nord, Wacker, Elkem and NEDO/Kawasaki. Schei [73] has

described a counter-flow solid–liquid reactor to remove boron by fractional extraction in a semi-continuous process in a patent assigned to Elkem ASA of Norway.

It has been demonstrated that phosphorus could be evaporated from a silicon melt under vacuum conditions [74, 75]. Miki *et al.* [76] have explained the thermodynamics of this process by reactions involving mono- and diatomic phosphorus in the gas phase:



Underscored symbols refer to dissolved element in liquid silicon as already defined in Section 5.3.2.

Silicon produced by carbothermic reduction is so to speak supersaturated in SiC when tapped from the furnace and may contain as much as 1000 to 1500 ppm(w) C. As this silicon is cooled down to the solidification temperature, the majority of this carbon precipitates out as SiC particles leaving around 50 to 60 ppm(w) in liquid silicon. Carbon removal from liquid silicon is therefore a two-step operation:

1. the removal of precipitated SiC as close to the solidification temperature as possible
2. the removal of dissolved C by oxidation to CO(g).

As already mentioned, SiC particles become effectively captured by the slag phase during oxidative refining in which the main objective may be to remove Al and Ca as industrially practised today or in a similar operation with the purpose of removing B or P. Depending on the temperature and the degree of slag/molten silicon intermixing, this treatment may give a product with 80 to 100 ppm(w) C. Other methods, which have been applied and proved effective at a temperature closer to the solidification temperature, are filtration, centrifugation or settling combined with slow cooling. Several studies have provided valuable contributions suggesting several methods, for example, settling in combination with directional solidification [77], filtration combined with oxidation [78], oxidative plasma [70–72] and decarburisation by inert gas purging or under vacuum [14, 78]. Klevan [14] has developed a mathematical model, which describes the kinetics of decarburisation when inert purging is applied. Mechanical removal is, however, not efficient enough to affect the substitution carbon. Stronger methods able to displace the equilibria, such as oxidative plasma and vacuum vaporisation, are believed to be more powerful techniques.

It is worth noting that these types of operation can all be carried out in carbon-lined ladles. The several steps dealing with the removal of dissolved carbon C from liquid silicon Si(l), however, has to be carried out in the absence of C and at a highest possible temperature in order to optimise the equilibrium and the kinetic conditions for the reaction:



A parallel reaction, which affects the silicon yield, unfortunately, also takes place:



The value of solid solubility of carbon in silicon is approximately 10 ppm(a), corresponding to the homogeneous distribution of substituted carbon atoms on silicon lattice sites. This type of carbon impurity is detected by infrared spectroscopy. Higher concentrations of carbon result in SiC precipitates of different size and morphology. This type of carbon is detected and analysed by combustion methods or secondary ion mass spectroscopy (SIMS).

5.7.2.4 Challenges and achievements

The improved carbothermic reduction of silica, followed by leaching and directional solidification, has the capability to produce silicon with sub-ppm concentration of all metallic impurities. Controlling the non-metallic elements, particularly B, P, C and O, at the level required for solar cell applications remains the major challenge for the metallurgical route. Unfortunately, there is no universal method for reducing simultaneously these critical elements. As a consequence, several refining steps are necessary, with the risk of reducing the silicon yield. Another risk is the recontamination by impurities from the reactants and the lining during handling and treatment of liquid silicon. Extensive studies were done on this route in the early eighties, but efforts since then have been considerably reduced. The Japanese program headed by NEDO is to our knowledge the most accomplished project representing this route (Table 5.10; [71]). On the basis of this project's results, Kawasaki has built a 60-MT pilot plant, but the economical feasibility of the route remains uncertain. In the NEDO process, metallurgical grade silicon is purified through

1. melting of silicon by electron beam and evaporation under vacuum
2. first directional solidification
3. remelting of silicon and gas treatment ($O_2 + H_2O$) assisted by a plasma torch
4. second directional solidification.

Table 5.10 Solar grade as obtained through upgrading metallurgical grade silicon by the NEDO method according to [71]

B [ppm(w)]	P [ppm(w)]	Al [ppm(w)]	Fe [ppm(w)]	Ti [ppm(w)]	O [ppm(w)]	C [ppm(w)]	Resistivity [ohm cm]	Lifetime [μs]
0.04–0.10	0.03–0.14	<0.01	<0.05	<0.01	<6	<5	0.8–1.2	>7.7

5.7.3 Simplification of the Polysilicon Process

The Union Carbide and Ethyl Corporation polysilicon processes (Sections 5.4.2 and 5.4.3) resulted from attempts to make the Siemens process more economical. Project goals were to meet a price target of 10 US\$/kg set in 1975 by the US Department of Energy (DoE). The Siemens process was fully developed around 1960, but polysilicon for electronic devices and other purposes had been produced since the forties. The Siemens process was the first design of a rational industrial process, which gained international recognition through rapid and broad licensing. At least a dozen processes had been developed prior to the Siemens process and coexisted with the Siemens process until the beginning of the seventies. Purity and high production rates based on semiconductor industry

demand were the primary criteria for the process design. Capital expenditure and energy consumption were considered secondary criteria. While large production quantities of ultra-pure polysilicon were available at acceptable prices for semiconductors, this price was too expensive for the development of low-cost solar systems. For solar cells, a process with reduced costs, reduced energy consumption and increased production rates, with purity levels not as important, is needed. Since several processes had been developed in the past, a review and re-evaluation of the silicon chemistry of these processes was suggested (see Tables 5.11 and 5.12).

Table 5.11 Historical processes to manufacture polysilicon (according to Strategies Unlimited [79])

Companies	Volatile silicon source	Reduction agent	Reactor type
Dupont	SiCl ₄	Zinc	Inside-quartz tube
Bell lab.	SiCl ₄	Hydrogen	Ta-filament
Union Carbide	SiHCl ₃	Hydrogen	Inside-quartz tube
Int'l Telephone	SiCl ₄	Sodium hydride NaH	Ta-filament
Mallinckrodt	SiI ₄	Hydrogen	Inside-quartz tube
Transitron	SiH ₄	Decomposition	Inside-quartz tube
Texas Instruments	SiCl ₄	Hydrogen	Outside-quartz tube
Foot Mineral	SiI ₄	Decomposition	Si-filament
Chisso	SiCl ₄	Hydrogen	Inside-quartz tube
Siemens	SiHCl ₃	Hydrogen	Si-filament
Komatsu	SiH ₄ SiHCl ₃	Decomposition	Si-filament
Motorola	SiHCl ₃	Hydrogen	W-filament
Phoenix Materials	SiCl ₄	Hydrogen	Si-filament
Texas Instruments	SiHCl ₃	Hydrogen	Fluidised bed spheres

Table 5.12 Polysilicon research projects stimulated by the objectives of low-cost solar cells programs after 1975

Companies/groups	Volatile silicon source	Reduction agent	Reactor type
Aerochem Res. Lab.	SiCl ₄	Sodium	Free space
Eagle Picher/General Atomic/Allied	SiH ₄	Decomposition	Fluidised bed
Battelle	SiCl ₄	Zinc	Fluidised bed
Hemlock	SiH ₂ Cl ₂	Hydrogen	Si-filament/rod
Union Carbide	SiH ₄	Decomposition	Free space
Union Carbide	SiH ₄	Decomposition	Fluidised bed
Ethyl Corp	SiH ₄	Decomposition	Fluidised bed
Motorola	Si _n F _{2n+2}	Decomposition	
NEDO	SiHCl ₃	Hydrogen	Fluidised bed
Rhône-Poulenc	SiH ₄	Decomposition	
Schumacher	SiHBr ₃	Hydrogen	Fluidised bed
SRI International	SiF ₄	Sodium	Solid separation
Westinghouse	SiCl ₄	Sodium	Free space
Bayer	SiCl ₄	Aluminium	Melt
Bayer	SiH ₄	Decomposition	Fluidised bed
Wacker	SiHCl ₃	Hydrogen	Fluidised bed

To make the process cost effective, the economics of both the production of the volatile silicon compound and its decomposition or reduction to elemental silicon had to be reviewed. Compared to the historical processes, the research projects did not discover radically new silicon compounds. Silicon halides $\text{SiX}_{4-n}\text{H}_n$ could apparently not be avoided. However, innovative methods were discovered to produce these silicon compounds. Metallurgical grade silicon remained in most cases the starting point, but silicon fluoride, obtained as co-products from phosphates leaching (fertilisers) and direct chlorination of natural silica to produce tetrachlorosilane, were envisaged as serious challenges. The research abandoned completely the concept of heated filament or seed rod that was clearly perceived as too expensive. Texas Instruments had demonstrated the benefit of the fluidised bed technology, that is,

- larger throughput
- lower energy consumption
- continuous operation
- lower capital expenditure.

Although the quality was not acceptable for making microelectronics devices, this was not a drawback for the development of the solar cell market.

In addition to the fluidised bed, free space reactor implying spontaneous seedless formation of solid silicon particles through homogeneous decomposition of silane has also been envisaged among others by Union Carbide [38].

None of these projects have resulted yet in establishing a new polysilicon route devoted to solar cells and decoupled from the electronic feedstock. The research has to a large extent developed and strengthened the classical polysilicon business by developing new products and processes to produce semiconductor grade silicon (Union Carbide, Ethyl Corporation). However, it is believed that for quality reasons, a significant portion of the Ethyl Corporation process production is still to find outlet in the solar market, making this product to some extent a prime solar grade polysilicon.

The other polysilicon producers have declared that by relaxing the production procedures and quality control they could, when excess capacity is available, produce specifically a solar grade polysilicon at reduced cost. It seems reasonable to expect a price reduction of approximately 35%. The same producers have underlined that specific investments to produce solar grade silicon by this route should not be expected because of too low profitability [80, 81].

At the time of writing, three projects aimed at developing a solar polysilicon route were in the process of being developed:

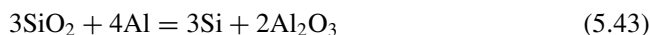
1. The German chemical company Bayer AG has for several years re-explored the decomposition of silane in fluidised bed reactor. The method combines the cost-effective synthesis of silane as in the Union Carbide process and the fluidised bed reactor as in the Ethyl Corporation process. The company has published the results of its basic assumption and made positive announcements [82–84]. Meantime, Bayer AG has withdrawn from the solar wafer business, which was the main driver for this feedstock development. To date it is therefore uncertain what the future of this project will be.

2. Another German company Wacker Chemie, which is one of the leading suppliers of electronic grade polysilicon and a great contributor to the development of materials to photovoltaics in the past, has decided to build a pilot plant to develop solar grade polysilicon by the reduction of trichlorosilane in a fluidised bed reactor. Under industrial conditions, each fluidised bed reactor should produce more than 500 MT/year and should be economical enough to meet the cost target of the solar cell industry.
3. The Japanese company Tokuyama Corporation, also a leading polysilicon manufacturer, has announced at a recent symposium its intention to develop a new deposition process using trichlorosilane in order to specifically produce solar grade silicon [85]. More technical details had not been presented at the time of writing this chapter. The reader is invited to consult later publications.

5.7.4 Other Methods

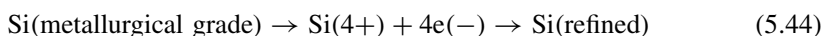
Besides the large avenues described above, one finds some other routes. The following processes are worth noting.

1. The aluminothermic reduction of silica



explored by Wacker [39].

2. The electrolytic transfer of silicon from an anode made partly of metallurgical grade silicon alloyed with Cu in (Cu₃Si-Si) to a graphite cathode through a liquid electrolyte made of KF:LiF:SiK₂F₆ as described by Olson *et al.* [86–88].



Although revisited by several R&D groups, these methods do not seem to have been the subject of extensive new programmes since the eighties.

5.8 CONCLUSIONS

At the time this handbook was written, silicon is the dominant PV material with more than 98% of cells and modules based on it. Crystalline technologies account for nearly 90%. We do not see new materials displacing silicon in the foreseeable future. The crystalline technologies require significant consumption of pure silicon. Purity requirements have not been exactly defined with the industry selecting silicon raw materials among the residuals from single-crystal pulling and second-grade polysilicon. At present, these sources are not sufficient to cover the rapidly growing demand from the solar industry. Polysilicon produced specifically for solar applications and prime-grade polysilicon are extensively used. This has the negative consequence of increasing the cost of solar cells and hence of slowing the market deployment of solar electrical energy. Research on a new dedicated route to solar grade silicon decoupled from the semiconductor business cycles has been going on for almost 30 years. Two directions still retain most of the attention of scientists and technologists: the further development of pyrometallurgical treatments of liquid silicon

and the simplification of the polysilicon processes. The crystallisation processes applied to silicon to produce the PV devices play a role in purifying and shaping silicon and should affect to a larger extent the development and the final definition of solar grade silicon. Quality and cost requirements have imposed strict limits to solar grade silicon. Capital cost is perceived as a significant part of the overall cost and adds to the barriers that need to be overcome.

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