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Review
Solar-grade silicon

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Various methods of manufacturing low-cost solar-grade silicon are reviewed. The methods include refining metallurgical-grade silicon, reduction of silicon compounds by metals and non-metals, transport and thermal decomposition processes. The materials are briefly characterized by the chemical analysis, resistivity measurements and efficiency of solar cells obtained from them.

1. Introduction

Semiconductor-grade silicon is widely used to manufacture highly efficient solar cells. Silicon tetrachloride or trichlorosilane is thermally decomposed and reduced with hydrogen to produce high purity silicon [1–9]. Since this process is complex and expensive, the use of semiconductor-grade silicon has been a major factor contributing to the high cost of solar cells. In general, the purity level of silicon required for cells could be considerably less than the purity levels of semiconductor-grade silicon. Hence, the cost of manufacturing solar-grade silicon for terrestrial utilization of solar energy can be significantly lower than the semiconductor-grade silicon. In this article we have attempted to review the status of various low-cost solar-grade silicon manufacturing processes and to characterize solar cells made from solar-grade silicon.

2. History of silicon manufacturing processes

Silicon occurs in nature chiefly as silica and silicates and makes up 25.7% of the earth's crust. In 1808, Berzelius obtained ferrosilicon by heating a mixture of silica, carbon and iron. Later, in 1811, Gray, Lussac and Thenard succeeded in preparing impure amorphous silicon by reducing silicon tetrafluoride with potassium. Soon after, Berzelius in 1824 purified amorphous silicon by removing the fluosilicates. Deville in 1854 first prepared crystalline silicon [10]. Later, silicon was produced by the thermal decomposition and reduction of silicon tetrachloride and trichlorosilane, electrolysis of a molten mixture of potassium fluosilicate and potassium fluoride or other alkali fluorides, and by the reduction of silicofluorides by sodium or aluminium. Copper has been used to obtain silicon by reaction with silica to form predominantly Cu_2Si and heating this with sulphur to form CuS and free amorphous silicon [11]. The most common commercial method of producing silicon is similar to a method by Berzelius wherein silica is reduced with carbon, usually in an electric arc furnace [12–17]. Other methods include the reduction of silicon monoxide with silicon carbide and the reduction of silicates with carbon or aluminium [18–23]. The first commercial process for the production of semiconductor-grade silicon used zinc to reduce silicon tetrachloride [23, 24]. The reduction of silicon tetraiodide, and tetrabromide, with hydrogen were also determined to be commercially feasible [25]. Currently, both silicon tetrachloride and trichlorosilane are widely used in the manufacture of hyper-pure silicon [1–9].

3. Definition of solar-grade silicon

Semiconductor-grade silicon is expensive, costing about $75/kg (US dollars) due to a number of process steps required to achieve the purity level of < 1 ppb metallic impurities. Although an unequivocal definition of solar-grade silicon does not exist to date, based on various investigations,

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some guidelines have been drawn. Wakefield *et al.* [26, 27] have provided a basis for the drafting of a solar-grade silicon specification. They have established that silicon raw material containing up to 120 ppm of a variety of common impurities can yield solar cells of at least 11.5% AM1* efficiency. They have listed the maximum impurity levels for solar-grade raw material silicon as follows: Al, 25 ppm; B and P, 0.01 ppm; others less than 5 ppm. They have, based on their cost analysis, obtained a linear relationship between purity and the cost as represented in Fig. 1. However, it should be remembered that the acceptable concentrations of impurities in solar-grade feedstock will depend on the growth technique as well as the cell fabrication processes involved. Hopkins *et al.* [28] have set a much broader range (1 to 1000 ppm) for a Czochralski growth operation. In this case, the tolerable feedstock impurity concentrations depend upon the melt recharges as shown in Table I.

As can be seen from Fig. 1, by reducing the purity requirements from <1 ppb to 10–50 ppm (semiconductor to solar grade), the cost of silicon could be reduced from \$70 to \$7/kg. Since it has been well recognized that low-cost solar cells suitable for large-scale terrestrial utilization can be made from slightly impure silicon at a price of about \$10/kg, Wafefield *et al.* identify the solar-grade silicon in the shaded area of Fig. 1. In principle, this purity and price range has been well accepted as the manufacturer's criterion for solar-grade silicon [26, 28].

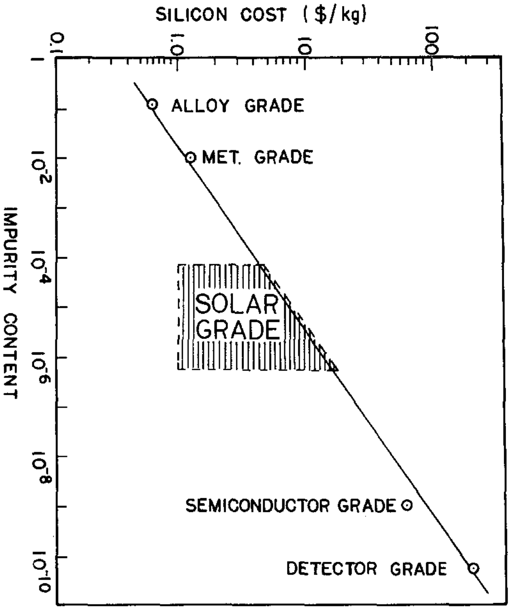

Figure 1 Relation between purity and the cost of silicon (from Wakefield *et al.* [26]).

4. Feasible methods of manufacturing low-cost solar-grade silicon

In the United States, the Department of Energy, in collaboration with Jet Propulsion Laboratory and the National Science Foundation, has had as an objective the development of the process technology for the production of low-cost silicon for solar cells in a large commercial plant by 1986, at a price less than \$10/kg (based on 1975 dollars). They have financially supported several organizations to evaluate all the possible economical means of manufacturing low-cost silicon. Under this scheme, Union Carbide, Dow Corning, Hemlock Semiconductor Corporation, SRI International Corporation, Aerochem Research Lab, Inc. and Crystal Systems, Inc. have demonstrated the feasibility of manufacturing low-cost silicon. In West Germany, Siemens and Wacker, and in Italy, Smiel, are developing processes to manufacture low-cost silicon. In Japan, under the Sunshine Project, Osaka Titanium, Komatsu Electronics and Shin Etsu Silicon are active in this development. The details of various processes are discussed in the following sections.

Graham *et al.* [29, 30] have made fundamental thermodynamic studies in detail to determine all the possible reactions for the reduction of silicon-bearing compounds. They have identified over 200 possible reactions, out of which about 148 reactions are thermodynamically feasible for the production of silicon. Among them, about 17 are considered to be economically suitable. The possible methods are:

(a) Pyrolysis of the compounds SiI_4, $SiHI_3$, SiH_2X_2, SiH_3X and SiH_4 below a temperature of 1725° C (where $X = F$, Cl, Br and I). Due to the high cost of these compounds and problems associated with corrosion, hence sustaining purity, this approach is not considered feasible at present.

(b) Reduction of silica by carbon. Metallurgical silicon can be produced and purified by various techniques. Even more directly, purer starting materials can be used to obtain a higher purity silicon product. These methods are economically attractive for producing solar-grade silicon.

(c) Reduction of SiO_2, SiF_4, $SiCl_4$, or $SiBr_4$ by various metals and rare earths is thermodynami-

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*Air Mass 1, 100 mW cm^{-2}, incident radiation.

TABLE I Tolerable feedstock impurity concentrations to achieve solar-grade silicon by Czochralski growth [27]

Impurity	One pull		Five sequential replenishments	
	atoms cm^{-3}	ppm	atoms cm^{-3}	ppm
Cu	1×10^{20}	2000	$2.2\ (10^{19})$	434
Fe	$9.3\ (10^{18})$	186	$2.0\ (10^{19})$	40
W	$8.8\ (10^{18})$	176	$1.9\ (10^{18})$	38
Zr	$< 5.0\ (10^{18})$	< 100	$< 1.1\ (10^{18})$	< 22
Co	$4.6\ (10^{18})$	92	$1.0\ (10^{18})$	20
Mn	$3.8\ (10^{18})$	76	$8.3\ (10^{17})$	17
Cr	$3.6\ (10^{18})$	72	$7.8\ (10^{17})$	16
Ta	$1.1\ (10^{18})$	21	$2.3\ (10^{17})$	4.6
Mo	$9.6\ (10^{17})$	19	$2.1\ (10^{17})$	4.1
P	$5.7\ (10^{17})$	11.4	$1.2\ (10^{17})$	2.5
Nb	$< 1.4\ (10^{17})$	< 2.8	$< 3.0\ (10^{16})$	< 0.61
Ti	$1.3\ (10^{17})$	2.6	$2.8\ (10^{16})$	0.56
V	$1.1\ (10^{17})$	2.2	$2.4\ (10^{16})$	0.48
Al	$3.3\ (10^{16})$	0.7	$7.2\ (10^{15})$	0.15

cally possible. However, due to the high cost of the materials, only Al and Mg are economical for reducing SiO_2 and Na for reducing SiX_4 (X = Cl, F, Br), and Zn for reducing $SiCl_4$.

(d) Reduction of the compounds SiO_2, SiF_4 and $SiCl_4$ with either CH_4 or NH_3 is feasible. Since the reactions begin in the temperature range 2100 to 2700° C, these methods are economically not suitable.

(e) Transport processes using the gaseous silicon compounds SiF_2 or $SiCl_2$ as intermediates to upgrade the metallurgical silicon are found to be economically desirable methods.

In the following sections, these possible methods for producing solar-grade silicon will be discussed.

5. Reduction of silica by carbon

Metallurgical silicon (MG-Si) appears to be an attractive choice as a starting material for the production of solar-grade silicon (SoG-Si). This material is commercially produced in electric arc furnaces at an estimated rate of about 600 000 tons per year globally and is available for an average price of US $1.20/kg. MG-Si is produced by reducing silica with carbon according to the overall reaction:

$$SiO_2(s) + 2C(s) \rightarrow Si(l) + CO(g). \qquad (1)$$

Coldwell [31] has made a thermodynamic analysis of this reduction process to obtain the optimum conditions. The raw materials used (especially the reductant mixture consisting of lignite, petroleum, coke, charcoal and wood chips) are the major source of various contaminants in the end product, and hence the purity level obtained in MG-Si is about 95 to 99%. A typical analysis of commercial MG-Si is given in Table II.

It has been well recognized that the high impurity concentrations listed in Table II prevent the use of MG-Si directly for photovoltaic applications. The concentration of the impurities exceeds the tolerable levels estabilished by Wakefield *et al.* (Table I). Davis *et al.* [32] have also shown the detrimental effect of the impurities in silicon on the performance of solar cells. Therefore, it is necessary to remove most of the impurities by some means and upgrade to SoG-Si with impurities at an acceptable level.

5.1. Refining metallurgical silicon by chemical methods

5.1.1. Acid leaching

In commercial MG-Si, the impurities, in the form

TABLE II Typical analysis of MG-Si

Concentration of impurities in MG-Si	
Impurity element	Concentration range (ppm)
Al	1000–4000
B	40–60
P	20–45
Cr	40–220
Fe	1500–6000
Cu	15–40
Mn	10–80
Ni	10–95
Ti	120–275
V	50–250
C	1000–3000
Ca	250–620
Zr	15–25

TABLE III Typical analysis of acid leached MG-Si [35]

Impurity	Impurity concentration (ppm)		Removal (%)
	Before	After	
Al	2080	150	93
B	20	14	30
Cr	180	5	97
Cu	22	13	40
Fe	2310	60	97
Mn	180	5	97
Ni	80	5	94
P	50	40	20
Ti	200	10	95
V	180	6	97

of complex compounds, lie largely in the intercrystalline boundaries. The simplest way of removing most of the impurities is to pulverize the silicon and treat the powder (50 to 70 μm particle size) successively with various acids or combination of acids including HCl, HF, H_2SO_4 and HNO_3. Tucker [33] used such a technique in early 1927. He prepared 99.94% pure silicon by successively chemically leaching fine silicon powders with aqua regia, hydrofluoric acid, sulphuric acid and finally with hydrochloric acid. These acids dissolved impurities such as iron and aluminium silicates and silicides of iron, calcium and magnesium as well as other impurities. He concluded that the degree of success depended on the particle size of silicon and length of acid leaching time. Gampel [34] obtained up to 99.99% pure silcon by acid leaching methods. Hunt *et al.* [35] obtained purer silicon (total impurities less than 400 ppm) by acid leaching pulverized silicon with aqua regia, hydrochloric acid and hydrofluoric acid at elevated temperatures for at least 12 h. A typical analysis of acid-leached MG-Si is given in Table III. Although the impurity reduction by this process is in excess of 90% for most of the elements, boron, copper and phosphorous are not removed effectively. Since the concentration of these elements, particularly

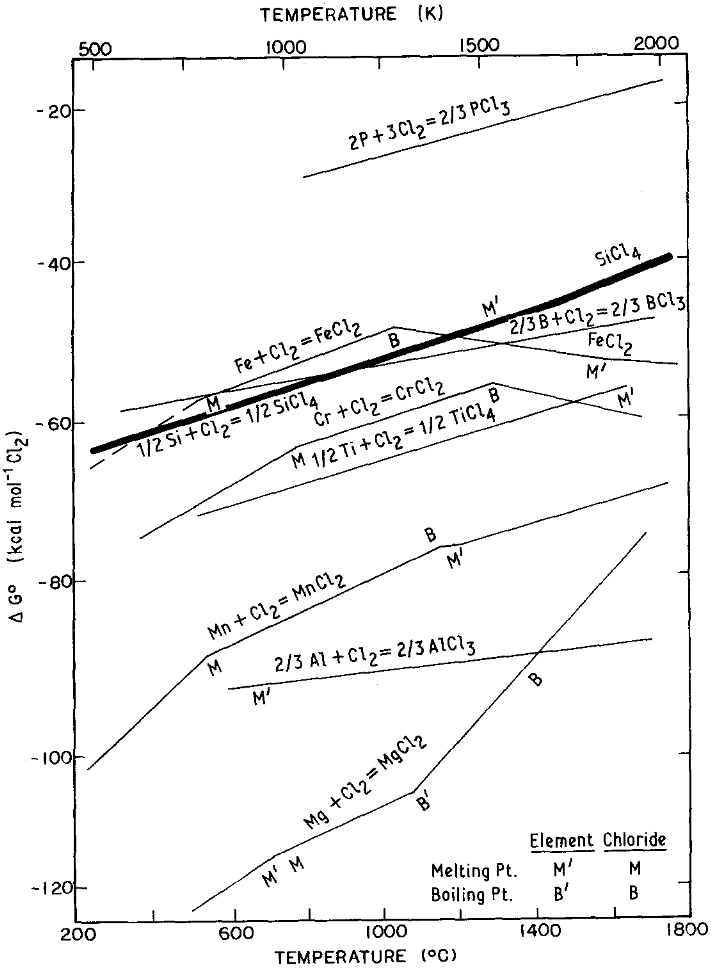


Figure 2 Standard free energy of formation of chlorides from their elements (from Graham *et al.* [29]).

the doping elements B and P, is much higher than the acceptable level for SoG-Si, the acid leaching method alone is not sufficient to purify MG-Si.

5.1.2. Reactive gas blowing

Reactive gas blowing is one of the common techniques practised by many MG-Si industries to obtain silicon with a purity level of at least 99.99%. The gases considered are Cl_2, O_2, $SiCl_4$, wet hydrogen and CO_2 or their combinations [36–49]. Either MG-Si or acid-leached MG-Si can be upgraded by blowing one or many gases, usually diluted with an inert gas, through molten silicon. With Cl_2 and its compounds, impurity chlorides are formed, which, due to their low melting and boiling points, are volatilized. Fig. 2 is the free energy versus temperature diagram for the formation of chlorides [29, 46]. It can be seen that Al, Mg, Mn and B chlorides are easily transported due to their low boiling points. Enk and Nickl [44] observed that substantial percentages of C, Ca, Mg, Al, B, P and Ti impurities in silicon are removed by this method. The free energy of formation of oxides from their impurity elements is given in Fig. 3 [29, 46]. Ca, B, Mg, Al and Ti are easily oxidized from the liquid silicon as expected from their large free energy values. Loss of silicon in either of the above treatments is found to be minimal [39]. Wet hydrogen, to some extent, reacts with dissolved boron to form hydrides which are very volatile at the melting temperature of silicon [50]. Thus, gas blowing is effective in removing Al, Ca, C, Mg, B, P and Ti from MG-Si. Other elements, due to their unfavourable thermodynamic properties, are not removed by the application of this method.

5.1.3. Slagging

This technique has been tried using $CaCO_3$, BaO, MgO, Al/SiO_2, CaO/SiO_2 and CaF_2/SiO_2 to obtain slags [47, 49, 51]. The amount of compound added is usually 1 to 5% of the silicon charge. The

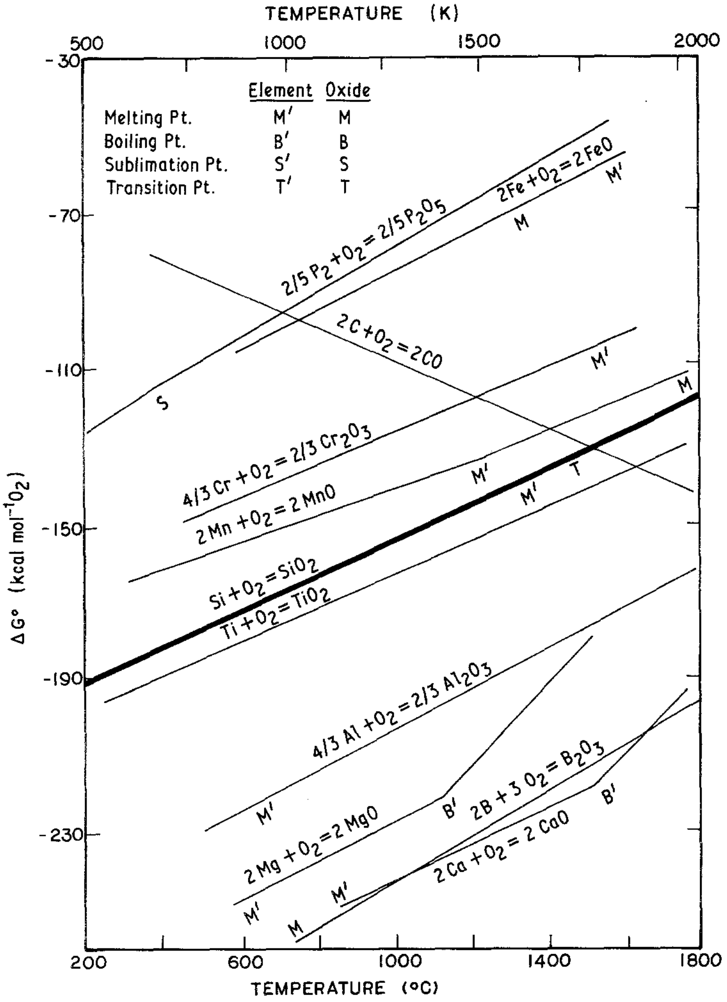


Figure 3 Standard free energy of formation of oxides from their elements (from Graham *et al.* [29]).

oxides react with silica crucibles to form low melting glasses which dissolve and extract certain impurities from the liquid silicon. The glasses adhere to the crucible wall, thus containing the impurities outside the melt. Impurity level reduction for some of the elements such as Ti, Mn, V and Al is about one order of magnitude.

It is apparent that a combination of these chemical methods is necessary to remove the spectrum of impurity elements. After these treatments, the purity level of silicon is fairly adequate and can be used as a feedstock material for directional solidification/crystal growth.

5.1.4. Use of pure raw materials

The most commonly used raw materials in MG-Si industries contain large amounts of impurities, particularly boron and phosphorus which are difficult to remove from MG-Si even after the purification steps described above. Thus, another approach for producing upgraded MG-Si is to use purer raw materials or to pre-purify the raw materials for the reduction of quartz by carbon. Hunt *et al.* [35, 52–55] developed such a process to produce high purity MG-Si which was then converted to SoG-Si by unidirectional solidification. They selected raw materials with low B and P contents, identifying silica from deposits in Arkansas (USA) and British Columbia (Canada) as suitable materials. In these deposits, the B content is less than 3 ppm, P is less than 10 ppm, Al is less than 40 ppm and Fe is less than 20 ppm. The reductants preferred are pelletized activated carbon, carbon black (both purified with Freon at 2500° C), and sugar-char using high purity binders such as starch, sugar, polyvinyl alcohol and cellulose. With sugar cubes, they found increased chemical reactivity since the sucrose is converted to a high-surface area sugar charcoal upon burning at the top of reactant mix. A specially designed electric arc furnace (called Direct Arc Reactor) with purified electrodes is used for the reduction process. The silicon yield obtained by this process is at least 70%. Alternatively, quartz sands can be purified by mixing with B_2O_3 and soda in a crucible and heating at 1200 to 1400° C to give sodium borosilicate glass which is separated into a quartz-rich phase at 100° C in 24 to 72 h. Acid leaching with HNO_3 yields pure SiO_2 which can be reduced with carbon to obtain pure silicon [56].

Amick *et al.* [57] in their patented literature have described a method to produce raw materials from rice hulls. The outer coating of commonly grown rice consists of cellulose, lignin and silica. The rice hull ash (13 to 15 wt% of the hull content) contains 95 to 99% SiO_2. By acid leaching these rice hulls in 50% semiconductor-grade HCl for 1 h, then pyrolyzing them at about 900° C for 30 to 60 min in a 1% anhydrous HCl/Ar gas stream, coked hulls with a carbon-to-silicon ratio of about 4:1 are obtained. Since the carbon-to-silica ratio is important for the efficient reduction of silica, the ratio is adjusted to just below 2:1 in a conventional fluidized bed combuster with high purity argon containing 5 vol% CO_2. At 950° C a constant reaction rate is maintained. This feedstock of coked rice hulls is then thermally reduced at 1900° C in a submerged arc furnace. The polycrystalline silicon obtained by this process contains total impurities less than 75 ppm, B and P each being less than 10 ppm. Another method to produce SoG-Si is to reduce the amorphous silica in purified rice husk ash by metallic magnesium powder at about 600° C followed by acid leaching and gas blowing purification processes [58].

TABLE IV Segregation coefficients for various impurities in silicon

Impurity	Segregation coefficient
Aluminium	2.0×10^{-3}
Antimony	2.3×10^{-2}
Arsenic	0.3
Bismuth	7.0×10^{-4}
Boron	0.8
Carbon	0.05
Chromium	1.1×10^{-5}
Cobalt	2.0×10^{-5}
Copper	4.0×10^{-4}
Gallium	8.0×10^{-3}
Indium	4.0×10^{-4}
Iron	8.0×10^{-6}
Magnesium	3.2×10^{-6}
Manganese	1.3×10^{-5}
Molybdenum	4.5×10^{-8}
Nickel	1.0×10^{-4}
Niobium	4.4×10^{-7}
Palladium	5.0×10^{-5}
Phosphorus	0.35
Silver	1.7×10^{-5}
Tantalum	2.1×10^{-8}
Tin	1.6×10^{-2}
Titanium	2.0×10^{-6}
Tungsten	1.7×10^{-8}
Vanadium	4.0×10^{-6}
Zinc	1.0×10^{-5}
Zirconium	1.6×10^{-8}

5.1.5. *Growth techniques*

One-step direct purification of MG-Si can be achieved to some extent by the available crystal growth techniques employing the directional solidification principle. These include the well-known Czochralski, float-zone melting, Bridgman–Stockbarger techniques, as well as the newer shaped crystal growth techniques such as edge-defined film-fed growth (EFG), web dendritic growth (WEB), ribbon-to-ribbon crystal growth (RTR), ribbon against drop pulling process (RAD), heat exchange method (HEM), and various horizontal growth techniques [59–61]. However, so far only Czochralski, float-zone and heat exchanger methods have been experimentally tried to achieve efficient SoG-Si from MG-Si [46–49, 52, 62–67]. The success of refining MG-Si by directional solidification techniques depends on the segregation coefficients of impurity elements in silicon. It is apparent from the list in Table IV that B, P and Al, due to their high segregation coefficients, are not easily removed from the melt. Unfortunately, they are dopants for silicon and uncontrolled amounts of these impurities make it difficult to specify bulk material properties for solar cell applications. In addition, it is extremely difficult to obtain homogeneous materials with high impurity levels. A combination of purification processes by chemical methods and directional solidification has provided the best results. Repeating the refining processes increases the purity but trades off in the final costs for silicon.

6. Reduction by metals and compounds

It is possible to produce SoG-Si using the processes of reduction of SiO_2, SiF_4, $SiCl_4$ and SiB_4 by several metals or compounds such as NH_3 and CH_4. Hunt [30] has listed the possible reactions to manufacture silicon by this method. The only method investigated to date for large-scale commercial production is the reduction of silicon halides by the alkali metals Na and K and by Zn. Dickson *et al.* [68] and Olson *et al.* [69] have taken advantage of continuous high temperature reactions of alkali metals and silicon halides to produce silicon in large quantities. It is known that the reaction of gaseous Na or K with silicon halides such as $SiCl_4$, $SiHCl_3$ or SiF_4 is highly exothermic and luminescent, and produces high adiabatic flame temperatures. The possible reactions are:

$$SiCl_4 + 4K\,(4Na) \rightarrow Si + 4KCl\,(4NaCl) \qquad (2)$$

$$SiHCl_3 + 3K\,(3Na) \rightarrow Si + 3KCl\,(3NaCl) + \tfrac{1}{2}H_2 \qquad (3)$$

$$SiF_4 + 4K\,(4Na) \rightarrow Si + 4KF\,(4NaF). \qquad (4)$$

The reagents $SiCl_4$ and Na are vaporized separately and admitted to the graphite reactor/collector assembly shown in Fig. 4. The flame temperature produced by this exothermic reaction is a function of pressure in the system as represented in Fig. 5. Although the adiabatic flame temperature falls in the range 1900 to 2200° C, the intense thermal emission from the silicon droplet fume quickly drops the temperature. The reaction products are NaCl(g) and Si(l). The Na salt exits as a gas from the reaction chamber and the silicon is present as a condensed phase. As the products exit from the reactor nozzle, a shock wave is generated upon impact in the collecting crucible which is kept at about 1425° C. Sodium vapour flows away from the crucible and the condensed silicon is collected in the crucible. The collection efficiency (ratio of the actual silicon collected to the total weight of silicon produced) ranges from 60 to 80% near 1420° C and strongly depends on the collector temperature. The resulting silicon contains as major impurities Na (300 to 600 ppm) and B

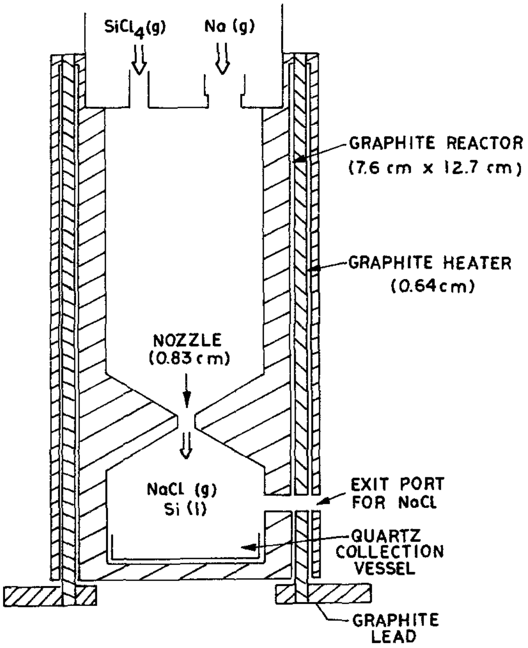


Figure 4 Graphite reactor and collector assembly for reducing $SiCl_4$ by Na (from Dickson *et al.* [68]).

TABLE V Summary of SoG-Si materials quality

Substrate	Concentration of major impurities present (ppm)	Resistivity range (Ωcm)	Efficiency of solar cells* (AM1) %, AR coated		Reference
			Diffused	Epitaxial	
MG-Si (pure starting materials)	B: < 8 P: < 5 Al, Fe: 50-100	0.10	8.0-12.0	–	[55]
MG-Si, reactive gases blown and Czochralski	B: 10 P: 20 Al: 2.5	0.06-0.20	–	–	[46, 52]
MG-Si, acid leaching, reactive gases blown, slagging and float-zone refined (FZ)	B: 20-40	0.40-0.60	9.8-13.0	–	[35]
MG-Si and Czochralski	B: 10-100 Al: 1-10 Fe: 1-10	0.02-0.06	4.0-6.9	–	[63]
MG-Si and *zone refined*	B: 1-10 Al: < 1 Fe: 1-10	0.02-0.06	7.5-8.8	–	[63]
MG-Si, reactive gases blown and Czochralski	Al: < 10 Ca, Fe, V, Ag: 10-100 Mn, Ti: < 10 (highly inhomogeneous)	0.14-0.32	–	–	[65]

MG-Si, acid leaching and directional solidification	N.A.	0.02-0.03	–	9.5	[62]
Refined MG-Si and Czochralski	–	0.06-0.10	8.5-11.1	7.5-10.6	[62, 110] [83]
MG-Si, gas blowing, slagging and directional solidification (twice)	B: 50-100 Al: 0.6-40 P: 5-11	0.01		10.3-12.9	[86]
MG-Si and Czochralski (twice pulled)	P: < 10 B: < 10	0.08	1.39-2.89	7.27-7.63	[84]
MG-Si and Czochralski (once)	B: 12-15 Al: 270	0.02-0.10	1.99	9.59	[64]
MG-Si and Czochralski (twice)	B: 12-15 Al: 2.40		6.57	9.93	
MG-Si, acid leaching and Czochralski (once)	B: 12-15 Al: 2.40		3.57	10.0	
MG-Si, acid leaching and Czochralski (twice)	B: 12-15 Al: 2.40		6.41	10.5	
MG-Si and HEM solidification	B: < 10 Al: < 2	0.045-0.090	7.2	–	[66]
Upgraded MG-Si (pure raw materials) and HEM solidification (twice)	B: < 8 P: < 3	0.15-0.20	3.8-12.33	–	[67]

* Efficiencies are normalized to AM1 (100 mW cm^{-2}) – AR coated cells.

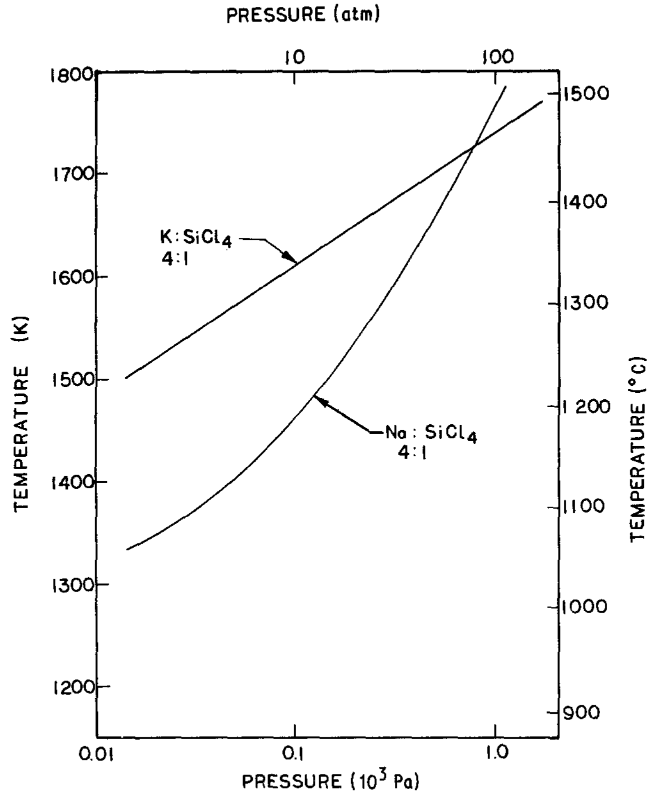


Figure 5 Adiabatic flame temperatures for alkali metal/$SiCl_4$ mixtures as a function of pressure. All reagents at 298 K, Na or K: $SiCl_4$ = 4:1 (from Dickson *et al.* [68]).

(< 25 ppm) with other elements less than 5 ppm each. Higher purity level is obtained in longer runs and by using purified collecting vessels and reactor materials.

Nanis *et al.* [70] have developed a method to produce low-cost silicon by reducing SiF_4 gas with Na. The basic principle is similar to the method described above. In this case, SiF_4 is obtained from H_2SiF_6 (fluosilic acid), a by-product of the phosphate fertilizer industry. When NaF is added to H_2SiF_6, about 99% pure Na_2SiF_6 (sodium fluosilicate) is obtained by the reaction:

$$H_2SiF_6 + NaF \rightarrow 2HF + Na_2SiF_6. \quad (5)$$

By thermally decomposing dry Na_2SiF_6 at about 700° C, SiF_4 is recovered by the reaction:

$$Na_2SiF_6 \rightarrow 2NaF + SiF_4. \quad (6)$$

Sodium chips are fed to the storage chamber and transferred to the reactor through a horizontal "hoe". The reactor, preheated to 400° C, is filled with SiF_4 gas to a pressure of 1 atm. Reduction of SiF_4 starts as soon as Na chips are dropped into the reactor according to the reaction:

$$SiF_4 + 4Na \rightarrow Si + 4NaF. \quad (7)$$

This reaction is highly exothermic and self-igniting above 150° C. The maximum adiabatic reaction temperature is achieved if the pressure of the SiF_4 gas in the system is about 1 atm and the reactants are in the stoichiometric ratio. Instead of solid Na, liquid Na at about 130° C can also be used. Fig. 6 shows the apparatus used for this process. The reaction products Si, NaF and some Na_2SiF_6 are collected at the bottom of the reactor. This product is removed and then heated to >1420° C in a graphite crucible using a standard Czochralski crystal-growth furnace. NaF reacts with SiO_2 at 1425° C. Hence, SiO_2 crucible is not preferred. Molten silicon particles are collected at the bottom of the crucible and NaF is cleanly separated to the upper layer. After cooling, the solid consists of two separate clean phases, with solid silicon collected at the bottom and solid NaF in an upper layer. Atlernatively, silicon can be separated by acid leaching the product with H_2SO_4 or HCl. Silicon obtained by this process contains as principal impurities Na (1.0 ppm) Cr (3 ppm), Fe (< 7 ppm), Ni (2 ppm), Cu (4 ppm), B (0.1 ppm), P (0.2 ppm), and other elements at < 0.5 ppm [71]. Impurities can be substantially reduced by refining these reduction processes and

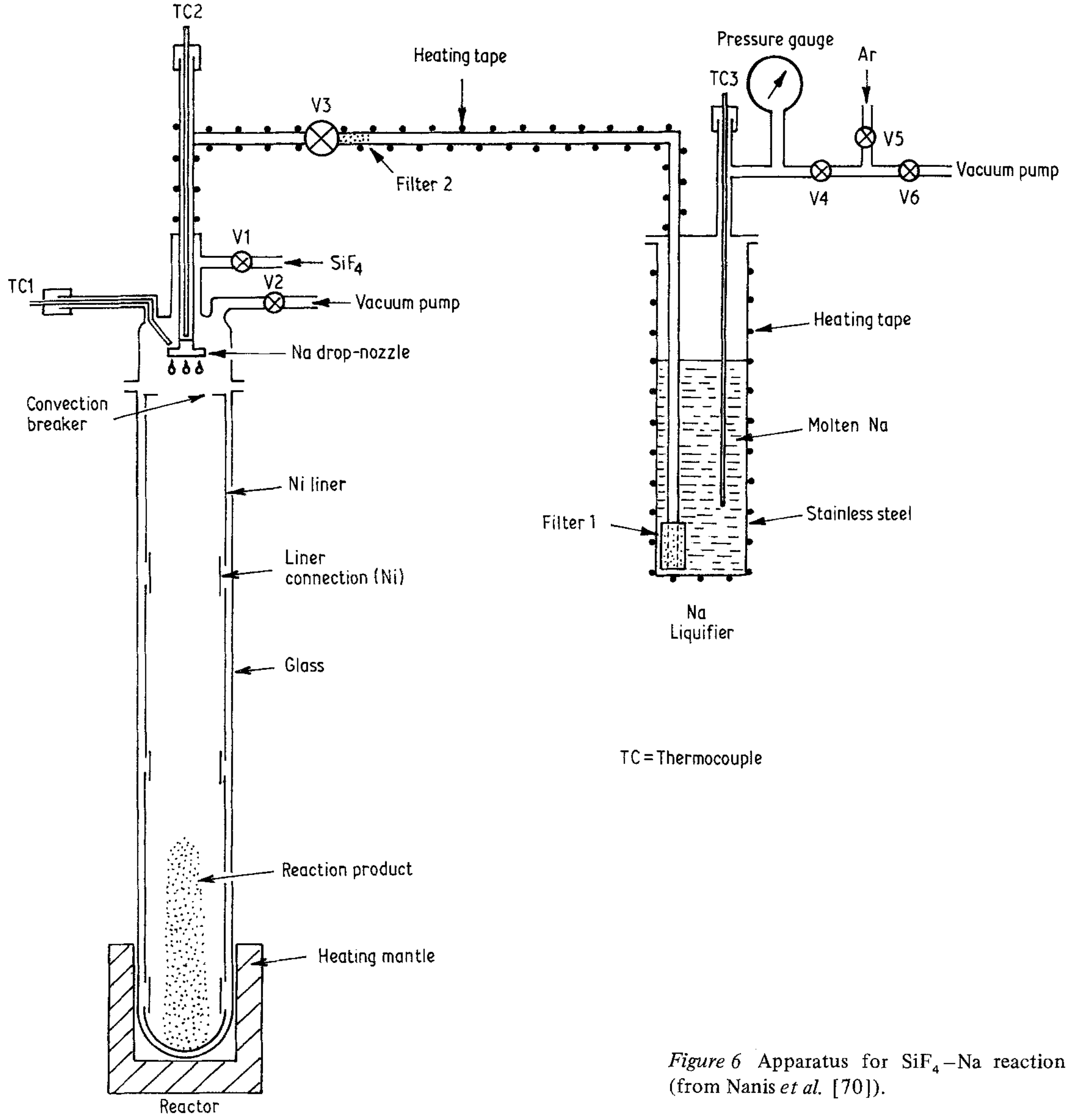


Figure 6 Apparatus for SiF_4–Na reaction (from Nanis *et al.* [70]).

carefully selecting materials for reactor/collector assembly. The possibility of reducing Na_2SiF_6 and SiF_4 using Mg has been reported, but, due to the large amount of booster required for such thermits reactions, the concentration of impurities in the silicon product is found to be rather high [72].

The earlier method of reducing $SiCl_4$ with zinc has been re-examined by Blocher and Browning [73]. The apparatus used for the preparation of silicon is given in Fig. 7. Both solid and vapour zinc-feeding systems were utilized. Silicon seed particles of about 250 μm in size were used as the fluidized bed. With solid zinc granules, no silicon was deposited on the seed particles. However, a mass of silicon needles was formed downstream of the bed. On the other hand, when zinc was fed as the vapour at temperatures from 900 to 1027° C, over 96% of the silicon produced was collected on the seed particle. The conversion efficiencies of $SiCl_4$ were in the range of 12 to 40%. Silicon and zinc chloride are obtained by the reaction:

$$2Zn(g) + SiCl_4(g) \rightarrow Si(s) + 2ZnCl_2(g, l). \quad (8)$$

Zinc and chlorine can be recovered electrolytically from the zinc chloride and then recycled. Boron concentration in the silicon is about 0.02 ppm and the major contaminants are Zn (3000 ppm), Fe (5 ppm), Ni (25 ppm) and Cu (4 ppm). The zinc

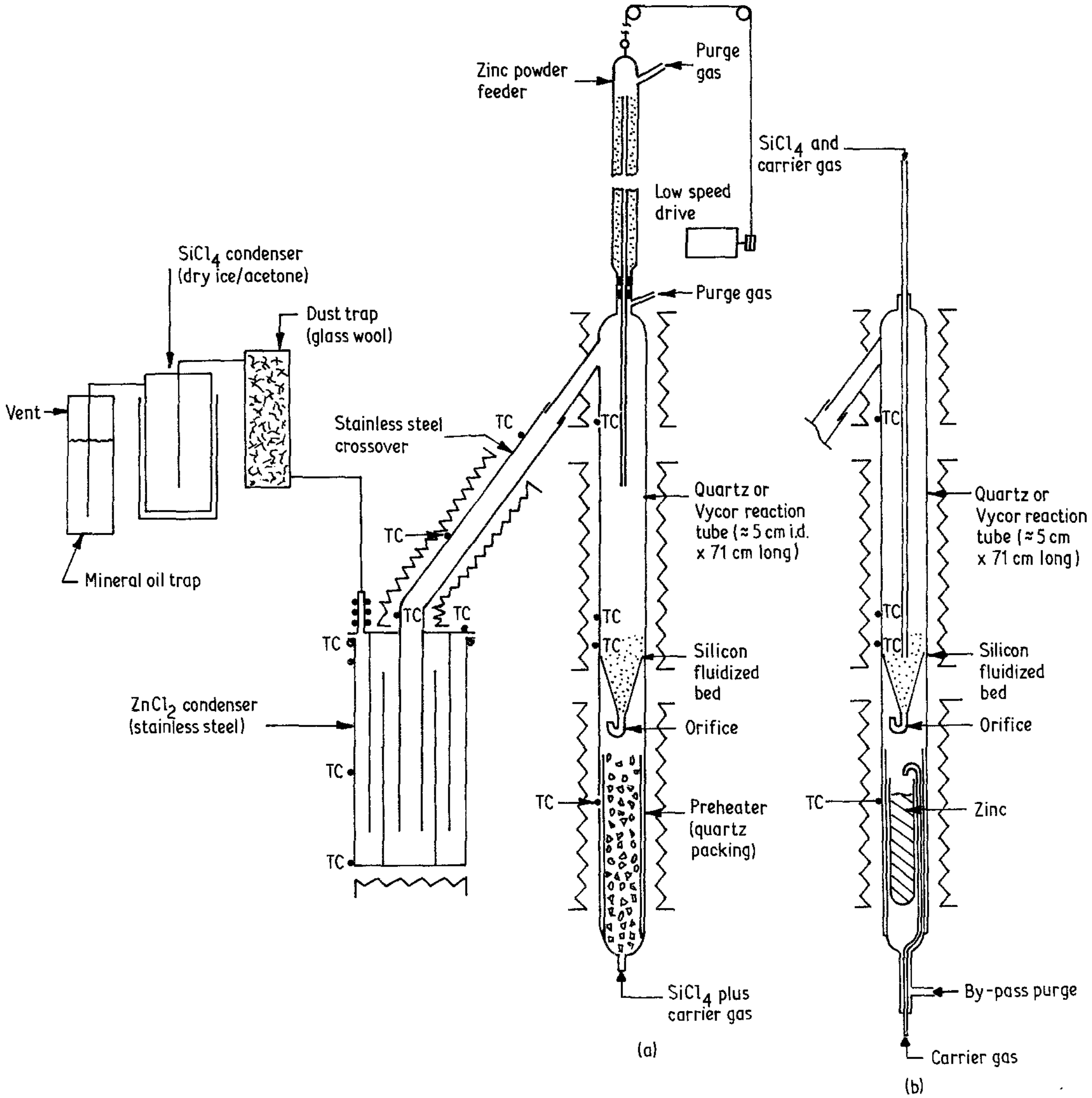


Figure 7 Schematic diagram of unit for the preparation of silicon by the zinc reduction of $SiCl_4$. (a) Solid zinc field; (b) Vapour zinc feed (from Blocher and Browning [73]).

may not be detrimental since in further processing at the melting point of silicon, the residual zinc, because of its high volatility, is expected to be evaporated [73].

7. Reduction and thermal decomposition processes

The prior art processes for producing semiconductor-grade silicon from trichlorosilane or silicon tetrachloride, either thermal decomposition or hydrogen reduction techniques are now being employed to produce solar-grade silicon. In a method described by Schumacher [74], a halosilane intermediate such as SiX_4, $HSiX_3$, H_2SiX_2, and H_3SiX (where X represents Cl, Br, or I) is formed by reacting MG-Si with a halogen or hydrogen halide at 400 to 800° C. This halosilane is purified by distillation, preheated to ~ 1000° C and injected into a continuous flow reduction reactor along with purified hydrogen heated to 900 to 1500° C. Then, heated silicon particles of selected size are fed to the reactor in order to catalyse the vapour-phase hydrogen reduction reaction. As an example, the chemical reaction involved for $SiBr_4$ is as follows:

$$\text{(MG) Si} + 4\text{HBr} \rightarrow \text{SiBr}_4 + 2\text{H}_2 \qquad (9)$$

$$\text{SiBr}_4 \text{ (purified)} + 2\text{H}_2 \rightarrow \text{Si (pure)} + 4\text{HBr}. \qquad (10)$$

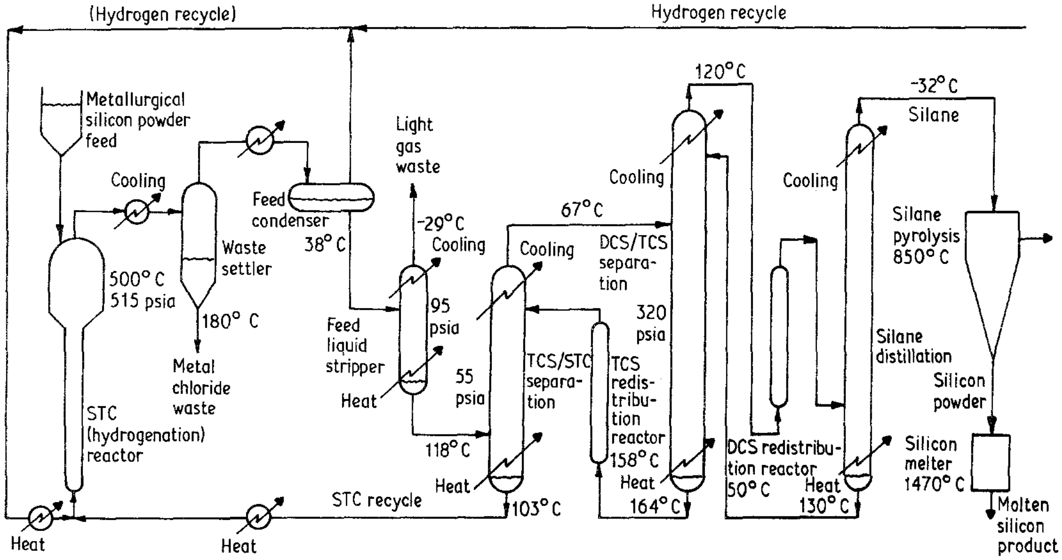


Figure 8 Silane production and decomposition process (from Breneman *et al.* [77]).

The hot silicon particles produced by this reaction are separated from gases by a cyclone-type solid gas separator and are slowly added to a pool of liquid silicon below the separator from which single-crystal silicon is continuously withdrawn. The by-products are purified and recycled.

Recently, Mui and Seyferth [75] have examined the kinetics of hydrogenation of $SiCl_4$ in detail. Breneman *et al.* [76, 77] have made a detailed investigation of a process capable of producing low-cost silane which can be pyrolysed to achieve solar-grade silicon. Fig. 8 shows a simplified view of this process. The sequence of the process is as follows.

(1) An equimolar mixture of the hot hydrogen and silicon tetrachloride ($SiCl_4$) is fed to a hydrogenation reactor operating at 3500×10^3 Pa (500 psig) and 500° C and containing a fludized bed of MG-Si and copper powder catalyst. At equilibrium conditions, trichlorosilane ($HSiCl_3$) is obtained by the reaction:

$$\text{(MG) Si} + 2H_2 + 3SiCl_4 \rightarrow 4HSiCl_3. \quad (11)$$

The hydrogen reactor produces a stream consisting of noncondensable gases (H_2, CH_4), condensable gases ($HSiCl_3$, $SiCl_4$) and vaporized or particulate impurity chlorides ($AlCl_3$, $FeCl_3$, BCl_3, PCl_5, etc.). The volatile salts precipitate on cool surfaces and are rejected in a scrubber system located adjacent to the reactor.

(2) The redistribution of $HSiCl_3$ is carried out in a packed-bed reactor at 70° C and 580×10^3 Pa (70 psig) in the presence of an ion-exchanger catalyst. $SiCl_4$ and H_2SiCl_2 (dichlorosilane) are produced by the reaction:

$$2HSiCl_3 \rightleftarrows SiCl_4 + H_2SiCl_2. \quad (12)$$

The product gases are separated by distillation.

(3) Redistribution of H_2SiCl_2 is carried out at 50° C and 3800×10^3 Pa (540 psig) by the following complex reactions:

$$2H_2SiCl_2 \rightleftarrows HSiCl_3 + H_3SiCl \quad (13)$$

$$2H_3SiCl \rightleftarrows H_2SiCl_2 + SiH_4. \quad (14)$$

$HSiCl_3$, in turn, produces $SiCl_4$ and H_2SiCl_2 by the reaction:

$$2HSiCl_3 \rightleftarrows SiCl_4 + H_2SiCl_2. \quad (15)$$

$SiCl_4$ is recycled and H_2SiCl_2 is utilized to produce more silane from H_3SiCl.

(4) Silane is separated from other gases by distillation columns. This purified silane is then vaporized and admitted to the injector nozzle of a quartz-lined free space reactor heated to ~ 800° C. Silane is decomposed into silicon and hydrogen according to the reaction:

$$SiH_4 \rightarrow Si + 2H_2. \quad (16)$$

The silicon powder obtained is of high purity with a very low boron level of about 0.04 ppb.

Ingle and Thompson [78] have investigated a process to produce high purity silicon continuously. Silicon tetrafluoride (which can be obtained economically by a method described by Nanis *et al.* [66]) is mixed with MG-Si and silicon dioxide and heated to ~ 1100° C to form silicon difluoride (SiF_2). Purification of MG-Si takes place at this stage of the process which is very effective for the removal of Al and B impurities. The presence of silicon dioxide is found essential for purification. Aluminium, for example, is removed by the following reactions:

$$4Al + 3SiF_4 \rightarrow 4AlF_3 + 3Si \qquad (17)$$

$$4AlF_3 + 3SiO_2 \rightarrow 2Al_2O_3 + 3SiF_4. \qquad (18)$$

In the continuation of the process, a small amount of silicon difluoride gas is first prepolymerized at a temperature between − 45 and 200° C to remove most of the remaining impurities present in the gas and then the bulk of silicon difluoride gas is polymerized at a lower temperature between − 45 and − 196° C. The silicon difluoride polymer is then heated to 100 to 300° C to form stable binary silicon fluoride homologues generally described to be of the form Si_xF_y. After distillation, the homologues are converted to pure silicon by contacting a substrate heated between 400 and 950° C for a sufficient length of time. The product silicon obtained can be amorphous, polycrystalline or single crystal, depending upon the substrate material and temperature.

8. Other methods

8.1. Epitaxial growth on MG and polycrystalline silicon substrates

D'Aiello *et al.* [79] have demonstrated that high-performance silicon solar cells can be fabricated using 25 to 50 μm epitaxial structure grown on single-crystal silicon. This concept has been utilized to improve the efficiency of polycrystalline sheet silicon, upgraded MG-Si and other silicon sheet materials such as EFG ribbon [65, 80–86]. The substrates are cleaned with ammonium peroxide and hydrogen peroxide mixture. The epitaxial solar cell structures are then grown by reducing dichlorosilane or trichlorosilane by hydrogen at about 1100° C in a standard horizontal reactor. Arsine or diborane diluted with hydrogen are used as doping gases. Epitaxial solar cell structures, 20 to 100 μm thick, are grown at a deposition rate of 1 to 5 μm min^{-1}. This process is considered economical due to the use of low-cost purified metallurgical and polycrystalline silicon substrates.

Calcote [87] has prepared strongly adhering films of amorphous and polycrystalline silicon on many materials by a reacting H/H_2 jet with $SiCl_4/SiHCl_3/SiH_4$. The possible reactions are:

$$SiCl_4 + 4H \rightarrow Si + 4HCl \qquad (19)$$

$$SiHCl_3 + 4H \rightarrow Si + 3HCl + H_2 \qquad (20)$$

$$SiH_4 + 2H \rightarrow Si + 3H_2. \qquad (21)$$

A non-equilibrium plasma jet is used to provide the source of hydrogen atoms via the dissociation of hydrogen gas in an electrical discharge. Hydrogen is partially dissociated and the resulting H/H_2 mixture is expanded through a nozzle where it is rapidly mixed with the other reactant to initiate the reaction. The jet is operated at a temperature ranging from 125 to 325° C with a discharge pressure ranging from 6.7 to 20×10^3 Pa (50 to 150 Torr). By placing a substrate material near the bottom of the reactor, silicon deposits/films are obtained. However, refinement of this process is needed in order to controllably dope the films and prepare photovoltaic amorphous silicon. Direct conversion of $SiCl_4$ or $SiHCl_3$ to SiH_4 or silicon by reaction with H/H_2 jet has also been accomplished but with a poor yield (< 20%). The impurities detected in these materials are predominantly Cl, Ni and Cr.

8.2. Electrodeposition

Recently, the electrodeposition process, as a low-cost method of production of SoG-Si, has received considerable attention. Alkali metal fluorides are frequently used as solvents in electrodeposition. Deville [88] first investigated the electrolysis of SiO_2 in NaF/KF. Monnier and Giacometti [89] obtained 99.99% pure silicon by electrolysis of solutions of SiO_2 in cryolite, Na_3AlF_6. Olson and Carleton [90] have recently described a process wherein an impure Si with copper addition is used as an anode and a molten salt mixture of LiF, KF and SiF_4 as the electrolyte. The alloy and electrolyte are contained in a vitreous carbon crucible serving as the anodic contact to the alloy. Graphite is used as a cathode. The operating temperature is typically about 700° C. Very small cell potentials are found sufficient to transport silicon from the anode to the cathode. The dissolved impurities in the anode that are more electronegative than silicon (e.g., Cu, B, P) remain in the anode and those that are less electronegative are transported to the cathode if they are present in solution at high concentrations. Segregation of these impurities at the anode may be accomplished by differential trapping. By this process, impurity concentrations of important elements like Al, B, Ti, Fe, V, Cr, W, Mo, and Cu are reduced to less than 1 ppm. Only, K, Li and F (from electrolyte) are present greater than a few ppm. In another technique, Olson and Kibbler [91] have used a molten tin cathode for extracting Si from SiO_2. The electrolyte is molten Na_3AlF_3 with additions of LiF, AlF_3 and BaF_2. The electrolyte and molten tin are immiscible and are contained in a vitreous carbon crucible with quartz lining. A purified graphite rod is used as an anode. At a decomposition voltage greater than 1.4 V, an Si^{4+} ion complex is reduced at and deposited in the molten tin cathode. Twinned platelets and well-formed polyhedra of silicon material are extracted from the molten tin. The major contaminants are Al, Ba, and Sn. In other electrode processes, polycrystalline silicon deposits can be obtained on silicon substrates from K_2SiF_6 dissolved in high temperature ($> 700°$ C) molten fluoride salts [92, 93]. Amorphous silicon deposits, at temperatures below 80° C, can be obtained from organo- and halosilanes, such as $SiHCl_3$, $SiHBr_3$, $SiCl_4$ $(ClC_3H_6)SiCl_3$ and $(CH_3)_3SiCl_2$ as silicon precursors in propylene carbonate electrolytes [92, 94]. The possibility of doping the electrodeposited silicon with B, Li and Ga and codeposition of n- and p-type dopants has also been investigated [95]. Elwell [96] also demonstrated that silicon can be electrodeposited from saturated solutions of SiO_2 in NaF/CaF_2 and KF/CaF_2 eutectic salts yielding fine elemental silicon particles at the cathode. However, these eutectic solvents offer no advantage over the silicon deposition using cryolite or LiF/NaF/KF eutectics.

8.3. Fractional crystallization

SoG-Si can be produced from MG-Si by fractionally crystallizing aluminium or any other metal silicon alloys containing sufficient quantity of MG-Si and by acid leaching the resultant crystal bed [97, 98]. The alloy is transferred to a crystallizer kept at a temperature above the liquidus. The temperature is then reduced to near the eutectic temperature and consequently silicon is precipitated from solution. The near-eutectic alloy is removed from the crystallizer and the process is repeated to remove additional quantities of metal from the crystal bed. The crystal bed is cooled to room temperature and residual metal is removed by acid leaching procedures. The silicon product can also be further purified by any one of the directional solidification techniques.

9. Characterization of SoG-Si material

The current commercial process for the production of polycrystalline silicon is by the vapour-phase deposition of silicon from a mixture of high-purity chlorosilane and hydrogen gas at high temperature. The polycrystalline silicon produced by this method contains impurities less than 1 ppb with a resistivity range of 30 to 100 Ωcm. Typical resistivity values for MG-Si are around 0.03 Ωcm mainly due to the presence of boron (40 to 60 ppm), phosphorus (10 to 45 ppm) and aluminium (1000 to 4000 ppm).

Standard purification techniques followed by directional solidification are capable of removing most of the impurities present in MG-Si but are inadequate for boron and phosphorus due to their high segregation coefficients. Even after Czochralski pulling and several float-zone passes, the B content in a chemically purified MG-Si is not reduced [35]. Typically boron is reduced to 7 ppm phosphorus to 5 ppm and other impurities to <5 ppm with a resistivity range for the product of 0.06 to 1.0 Ωcm. It is not clear whether the Theurer's method [50] of removing boron from semiconductor-grade silicon by hydrogen water-vapour treatment coupled with zone refining can be effectively applied to MG-Si or SoG-Si.

It is generally thought that an acceptable resistivity range for p-type silicon materials to be used for solar cells is from 0.1 to 2.0 Ωcm. This range criterion may be modified according to crystal growth and cell processing techniques. For example, Iles and Soclof [99] have demonstrated that the efficiency of solar cells reaches a maximum in the resistivity range 0.1 to 0.3 Ωcm for Czochralski-grown materials.

The remaining impurities in SoG-Si can also degrade the solar cell performance. Davis *et al.* [32] have studied the effects of impurities on solar cells fabricated on single-crystal wafers from Czochralski or float-zone grown material doped with specific impurities and impurity levels. Fig. 9 represents the influence of each impurity on the efficiency of a p-type solar cell. The effect of combinations of impurities on the efficiency is rather complex and is not necessarily simply an

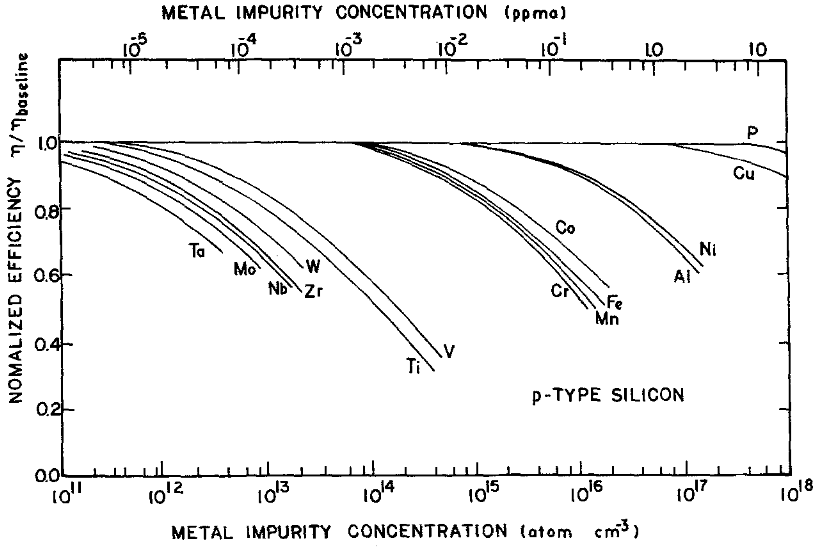


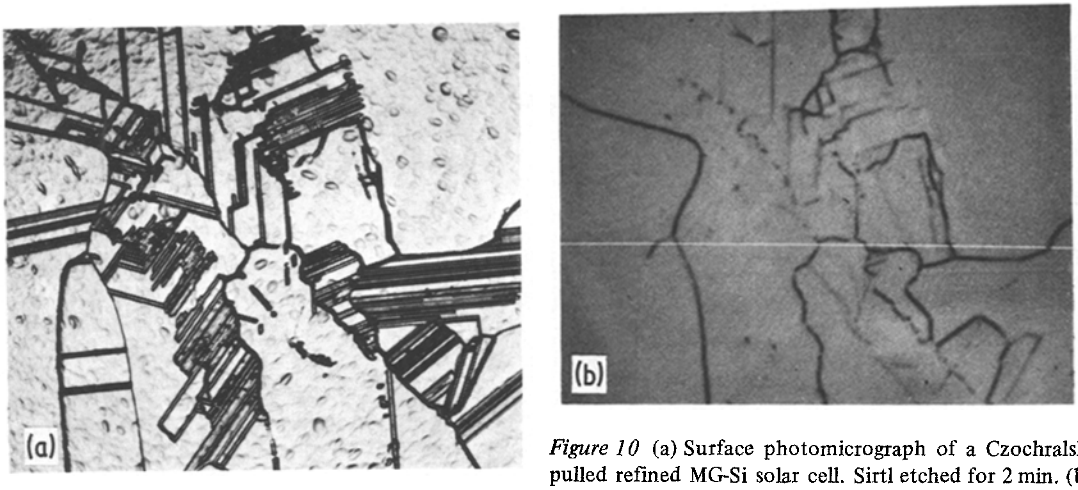
Figure 9 Model-derived impurity–performance curves for single metal contaminants in p-type silicon (from Hopkins *et al.* [28]).

additive degradation. Even so, the result remains as an adverse effect on efficiency.

Although reference is made throughout to SoG-Si, the definition of this grade of materials is not unambiguous. Certain impurities are generally deleterious to solar cell behaviour; however, the tolerable level of impurities depends on the growth technique and the specific processing procedures. To some degree, this tolerance level could be affected by the carbon and, more so, by the oxygen levels. Intrinsic gettering via oxygen interactions with defects and impurities has been extensively studied in single-crystal silicon [100–112]. Many of these effects are also observed in the polycrystalline sheet-grown materials used in solar cell fabrication [103, 104]. Thus, along with the impurities commonly discussed in SoG-Si, the carbon and oxygen concentrations need also to be considered.

An additional perturbation is the difficulty in chemically characterizing material with contaminants in the ppb to ppm range. Conventional analytical techniques suffer from various limiting features. In many cases, methods such as mass spectrometry, Auger spectroscopy, ion microprobe analysis, analyse only a very small volume of material. Thus, although the detection levels for these methods are quite sensitive, the concentration of contaminant excited with the matrix element may be too low for detection. Also, because of the small sampling volume, the concentration determined may not be representative of the bulk composition if inhomogeneous impurity distribution exists. This is particularly so for polycrystalline materials where impurities tend to segregate to boundaries. Other methods which analyse the bulk, such as emission spectroscopy or activation analysis, suffer from a decrease in sensitivity, or from interference among the elements.

Another factor to be considered here is the structural defects introduced in the SoG-Si cells. Single crystallinity is lost when impurities exceed certain concentration levels. For instance, at carbon concentrations in the melt in excess of 5×10^{18} ($k_0 \approx 0.5$) single-crystal Czochralski growth cannot be maintained [106]. This is also demonstrated in sheet growth techniques such as EFG of silicon ribbon where the effective segregation coefficient for impurities is about 1, and typical concentration of substitutional carbon is 3×10^{18} atom cm^{-3} [105]. The equilibrium defect structure obtained in this growth method is similar in properties to the polycrystalline growth initiated by an impurity excess. The predominant defects in polycrystalline materials are twin boundaries, grain boundaries, dislocations and inclusions. These defects are very common in SoG-Si, where impurities tend to segregate along the boundaries and as precipitate inclusions. In general ~ 90% of the impurities which could be electrically active in silicon appear to be neutralized by some interaction during growth. Extensive research has



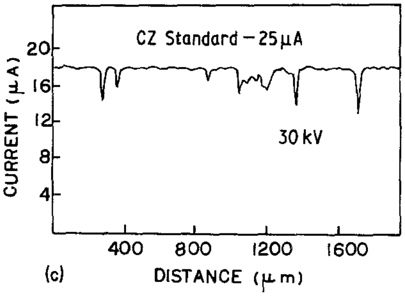


Figure 10 (a) Surface photomicrograph of a Czochralski pulled refined MG-Si solar cell. Sirtl etched for 2 min. (b) Corresponding EBIC image measured with a 30 kV electron beam. (c) EBIC line scan.

been done to study the electrical activaties of these defects and their effect on the conversion efficiency of solar cells [107–113]. Fig. 10a is a typical example of the surface morphology of a Czochralski pulled refined MG-Si and in Fig. 10b and c and electron-beam induced current (EBIC) image of the same area with a line scan is shown. The dark regions in the EBIC micrograph are recombination centres depicting the degradation occurring in this solar cell due to these boundaries. It can be seen that all the boundaries are not electrically active. Since it is beyond the scope of this paper, the electrical activities of other defects are not discussed here.

In spite of all these defects and impurities, solar cells with efficiencies varying from 7 to 13% (AMl) have been made from SoG-Si. Table V summarizes the results which have so far appeared in the literature. It should be noted that the materials are highly inhomogeneous and the tabulated values do not necessarily represent an overall average value for efficiency.

10. Conclusions

The methods discussed herein to produce solar-grade silicon are constantly being re-examined and refined to provide material being utilized to produce SoG-Si at a commercial scale at present. Therefore, we have not attempted to compare the merits, demerits, and cost analysis of these processes. The success of a method depends not only on producing silicon to make better than 10% efficient cells, but also on the capability of manufacturing them at a very large scale, economically, for terrestrial utilization. With the concentrated effort and research being carried out in this field, this goal should be achieved in the near future.

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