

Polysilicon vs. upgraded metallurgical-grade silicon (UMG-Si): Technology, quality and costs

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ABSTRACT

Throughout the severe plummet of PV prices that took place during 2008–2012 as a result of overcapacity, the polysilicon sector suffered a major adjustment of costs and capacity to face the reduction in prices and the mismatch between demand and supply. In 2012 that significant drop in prices provoked the bankruptcy of many polysilicon producers, with only the large and efficient players still surviving. However, there was also an impact on the (at that time) promising and immature industry of metallurgical purification of metal silicon, also known as *upgraded metallurgical-grade silicon (UMG-Si)*. The strong selling point of UMG-Si producers – the production costs – was no longer an asset, leaving UMG-Si with nothing but its weakness – the quality. The generation costs for solar energy are currently comparable to those for conventional fuels. The solar industry is self-sustaining and is not dependent on government subsidies. In this current situation, the industry requires an updated comparison between the two main routes of silicon purification and their products, which is the aim of this paper. The first route is the *indirect route (or chemical route)*, in which the metallurgical-grade silicon (MG-Si) is transformed into a silane (typically trichlorosilane TCS, or silane MS), which is refined and finally introduced into a chemical vapour deposition (CVD) reactor where the silicon is deposited. The second route is the *direct route (or metallurgical route)*, whereby the silicon is purified by means of metallurgical processes. The principal technologies within each route, along with their main advantages and challenges, are briefly described in this paper. Subsequently, the inherent quality of the product and the costs associated with each purification route are assessed by compiling the producers' published information and the authors' analyses.

Introduction

According to PVInsights [1], the spot prices of polysilicon have dropped from \$300/kg in 2006 to \$14/kg in 2015. Because of the high cost of the traditional polysilicon production processes that were industrially available when the demand of silicon started to be significant, back in 2004, a lot of effort in the past ten years has been put into improving costs and quality of materials aimed at the PV industry. The extremely high spot prices reached by polysilicon in the past decade (see Fig. 1) promoted big

investments in solar-grade silicon (SoG-Si), both for commercial production and for R&D activities.

High-purity silicon production processes can be divided in two main groups: the indirect or *chemical* route, and the direct or *metallurgical* route. In the indirect route, silicon is transformed by chemical reactions into a compound that can be purified by conventional chemical techniques, such as distillation. The silicon is then recovered as a pure solid from the selected compound by a chemical vapour deposition (CVD) process,

for which the two predominant technologies are Siemens and fluidized bed reactor (FBR) deposition. In the direct route, a sequence of metallurgical techniques, such as slag treatment or segregation, is applied in order to remove impurities from solid or molten silicon.

The main drawback of the Siemens-type processes for polysilicon production has traditionally been their very high specific energy requirements: typical energy consumption values range between 60 and 120kWh/kg, of which at least 45kWh/kg can be attributed to the CVD process. The use of chlorosilanes and silane as intermediates requires special handling precautions that also need to be considered. Additionally, high capital expenditures are required for establishing a new facility, along with rather long periods of planning, engineering and construction [2].

The direct route can produce different qualities of silicon, all of them called *upgraded metallurgical-grade silicon (UMG-Si)*. However, producers have refused to accept this term because, originally, the quality (99.99%) of UMG-Si was not pure enough and it had to be blended with polysilicon for PV applications. Nevertheless, in the last ten years, important industrial

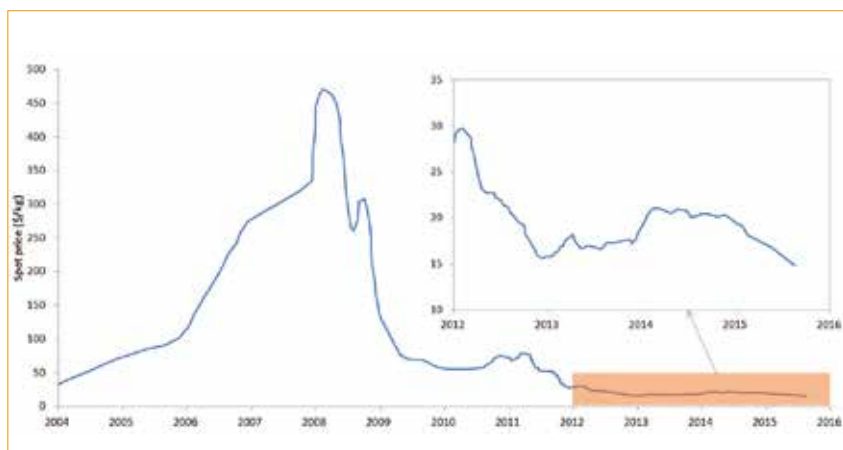


Figure 1. Evolution of polysilicon spot price.

developments in the direct route have led to improvements in silicon quality, resulting in a level of ‘silicon for PV applications’, or solar-grade silicon (SoG-Si > 5N) [3]. On the other hand, in their pursuit to reduce production costs, polysilicon producers have lowered the quality of their electronic-grade silicon (EG-Si), down to that of SoG-Si. Just to differentiate the provenance of SoG-Si, *UMG-Si* refers to the SoG-Si derived from metallurgical cleaning, and *polysilicon* refers to the SoG-Si derived from chemical cleaning. Under the polysilicon denomination, both Siemens-type silicon chunks and granular silicon coming from FBR deposition reactors are included.

“A balance should be established between silicon feedstock cost, maximum allowed impurity concentrations, and cell performance.”

A debate regarding the quality needed for PV applications has been ongoing during the past few years [4]. The specifications of this quality are still not yet defined in an unequivocal manner because of the fact that, excluding the boom period, very high-quality silicon has been available for PV applications, and so no real need to use other materials has arisen. A balance should be established between silicon feedstock cost, maximum allowed impurity concentrations, and cell performance. Since the effect of different chemical elements on cell performance varies, an oversimplification of the specifications leads to the wrong idea that only ultrahigh-purity silicon can be used for all solar PV applications. As the SoG-Si production sector reorganizes, the oversupply situation in recent years will give way to a balanced situation in which this material will not be available in such large quantities as in the past three years; new opportunities will therefore arise for low-cost materials.

Traditionally, the arguments against UMG-Si have been related to quality. It is true that the concentration of metals and dopants is higher in UMG-Si than in polysilicon; nevertheless, this level could be low enough for PV applications. As a result, that lower quality forces UMG-Si producers to sell the silicon at a lower price than polysilicon in order to make it attractive to the rest of the value chain. For example, in their work related to cells manufactured from

UMG-Si and polysilicon, Krause et al. [5] introduced the possibility of implementing a phosphorus gettering step to reduce the effects of some of the typical contaminants present in UMG-Si wafers, especially transition metals [6]. In that study, it was assessed that the price of UMG-Si should be 6 to 18% lower than polysilicon in order to counterbalance the extra cost of the gettering process; this equates to 6% in the case where the efficiencies of the solar cells made of polysilicon and UMG-Si are the same.

Technology

Metallurgical route

A variety of purification processes are involved in the metallurgical route [7]. None of them in isolation is efficient enough to achieve an adequate purification of metallurgical-grade silicon (MG-Si); different combinations of them, however, lead to purification sequences that can transform the MG-Si to SoG-Si. The most important processes are:

- Slag treatment of the silicon melt
- Vacuum degassing of the silicon melt
- Plasma treatment
- Acid leaching
- Purification of liquid silicon using gases
- Refining silicon from Al–Si melt
- Segregation during solidification

a) Slag treatment of the silicon melt

It is particularly difficult to eliminate boron by directional solidification because of its segregation coefficient in silicon (0.83) [8]. Additionally, its low vapour pressure makes it difficult to evaporate it from the silicon melt in a vacuum degassing process [9]. Consequently, slag treatment is the common method used for boron removal, although it also reduces the concentration of other impurities, such as metals and phosphorus, in the silicon melt.

Also known as *liquid–liquid extraction*, slag treatment is based on the higher solubility of certain impurities in a slag melt than in liquid silicon, or on the reactions of those impurities with some of the slag’s components to form more stable compounds. In this high-temperature process, the slags can be added to the silicon before or after its melting, depending on their composition. Once the slags are melted, they are immiscible with liquid silicon. The impurities are then dissolved in the slags, which, at the end of the process, can be extracted from the molten silicon. There are

different compositions of slags – the ones mostly used are oxides and fluorides.

b) Vacuum degassing of the silicon melt

Although phosphorus responds better than boron to directional solidification (segregation coefficient of P is 0.35), it is still difficult to reduce the P concentration to the levels required for the PV industry. Vacuum refining has been demonstrated to be a reliable technique for that purpose, and a large number of publications have contributed to its industrial implementation [10–13]. This technique consists of phosphorus evaporation from the silicon melt, in the form of P(g), P₂(g) and to a lesser extent P₄(g) [14]. The stirring of the silicon melt is therefore of major importance in order to allow an optimum transport of phosphorus to the melt surface.

The industrial application of these processes has been already developed with good results [15]. One company that currently uses vacuum degassing as one of the refining steps is Sinosi Group Corporation [16].

c) Plasma treatment

Plasma treatment consists of using argon gas to generate plasma, in conjunction with reactive gases that contain oxidizing species. A plasma torch is formed inside a tube and directed onto the melted silicon surface. The silicon purification begins when the reactive gases – oxygen and hydrogen – are injected into the plasma torch. Volatile species, mainly BOH and BO, are produced and extracted, with the consequent reduction of boron in the silicon melt.

The French Photosil consortium uses this process together with different directional solidifications and the selection of the raw material (MG-Si) [17]. One of the difficulties of this technique is the P concentration of the final product, which has to be under 0.6ppm_w, as the directional solidification processes, by themselves, are not efficient enough for P reduction [18].

d) Acid leaching

During silicon solidification, the impurities with lower solubility in solid silicon than in liquid silicon tend to precipitate at grain boundaries and interstitial positions [19]. The addition of CaO and/or CaCO₃ promotes the formation of Ca compounds between the silicon grains; those compounds are also formed by the impurities present in the silicon [20]. The solidified silicon is then mechanically reduced to smaller pieces, which have been broken preferably along the grain

boundaries, exposing the impurities to a subsequent chemical etching with acids (HCl, HF/HNO₃, etc.).

Acid leaching has been demonstrated to be efficient at removing metals – such as Fe, Al, Ca and Ti – while P has been reduced by as much as 80% [21]. Nevertheless, acid leaching is not an efficient process for boron reduction.

e) Purification of liquid silicon using gases

This purification procedure is based on the reaction of certain gases with the impurities in silicon to form slags or volatile species [22]. The gas treatment of the silicon melt is already a common process in MG-Si production. When the MG-Si silicon melt from the submerged arc furnace (SAF) is poured into the ladle, oxygen gas can be introduced, thus promoting the stirring of the melt and oxidizing the silicon to form SiO₂, which acts as a slag to which the silicon impurities are transferred from the melt.

The same principle has been applied to UMG-Si production. Besides O₂, other gases (such as chlorine) can be used for silicon refining. A mixture of O₂ and hydrocarbon (oxy-fuel) has been shown to be an effective method for B reduction [23].

f) Refining silicon from Al–Si melt

This is a metal–metal extraction process based on the fact that the melting point of Al–Si alloy is lower than that of Si, and that the solubility of Al in Si is low. A mixture of Si and Al melts at a lower temperature than Si, which means the energy needed to make the process is less. After melting in a crucible, the solution is slowly cooled and the silicon precipitates and grows in a flake shape.

In addition, the solubility of impurities in Al–Si alloy is higher than in Si [24]. The Al–Si alloy, which is still in a liquid state, is poured out from the crucible, leaving behind the silicon flakes. The silicon flakes, which are coated with a thin layer of Al, are then etched in chemical baths to remove the coating. To the authors' knowledge, Silcor Materials is the only company that uses this technique.

g) Segregation during solidification

The segregation method is based on the impurities' segregation coefficient k_i during a directional solidification (DS) of silicon; the segregation coefficient is the ratio between impurity concentration in the solid and the concentration of the same impurity in the melt. This means that the further the coefficient is from unity, the more effective is the segregation of

impurities. For example, metals have a very low k_i ; consequently, during a directional solidification the impurities tend to accumulate at the end of the ingot, and this part of the ingot is discarded. However, B and P have a coefficient close to unity, thus making DS an inefficient process for B and P reduction.

DS is a common technique in all the metallurgical refining processes, and can take place during casting in the SAF furnaces or within the refining process itself. In the next step of the value chain, namely crystal growth, DS is indeed the process used to produce silicon ingots; therefore there is an additional purification in this step [4].

There are a wide range of furnaces and castings that take advantage of the segregation properties of certain elements within silicon. A rapid segregation can be carried out during casting, allowing the silicon melt to cool down naturally while a magnetic stirring of the melt is performed by induction. This stirring promotes the transportation of impurities to the crystallization front and enhances their segregation. In the case of silicon crystallization, there are other examples of directional solidification, such as the use of furnaces quite similar to those used for silicon growth, based on the heat exchange method. However, this is an expensive process, which takes place in a vacuum or inert environment, and serves only for the advanced stages of silicon purification.

Other approaches

Other metallurgical processes have not been considered here, because of their poor, or lack of, representation in the industry. Alternative approaches to purifying silicon include the chemical purification of silicon- and carbon-containing compounds that are later transformed into high-purity raw materials used for MG-Si production, specifically silica (SiO₂) and carbon. A case in point is the ChemArc Process developed by RSI Silicon Products LLC, in which sodium silicate is thoroughly purified by chemical techniques and subsequently reduced with pure carbon in a modified SAF furnace, to yield a solar-grade product.

Chemical route

The indirect, or chemical, route for high-purity silicon production has been used since 1950, when the first applications for this material within the semiconductor industry appeared. The evolution of the technology has been slow for several decades, since electronic devices use only a tiny

amount of material. Today, the total demand for electronic-grade silicon (EG-Si) is approximately 30,000 MT/year – one order of magnitude lower than the demand for solar-grade.

Current commercial chemical technologies for the purification of silicon can use trichlorosilane (TCS, SiHCl₃) or silane (MS, SiH₄). The processes have in common the fact that the selected silicon compound undergoes a CVD reaction at a high temperature, which can be carried out by means of the traditional Siemens reactors or the less widespread FBR technology [25].

The commercially implemented processes in use today are, in essence, different combinations of precursor synthesis and by-products recycling, together with various deposition alternatives:

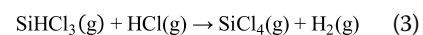
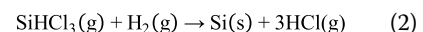
- TCS Siemens with direct chlorination (DC) and silicon tetrachloride thermal conversion
- TCS Siemens with hydrochlorination (HC)
- MS Siemens
- MS FBR

a) TCS Siemens with direct chlorination (DC) and silicon tetrachloride thermal conversion (Fig. 2(a))

MG-Si is converted to trichlorosilane (TCS) by a reaction with hydrogen chloride, according to the following equation:



Metallic impurities included in the MG-Si are transformed into their corresponding metal chlorides, remaining in solid phase after the reaction takes place. Boron and phosphorus are also transformed into their chlorides, which are gases in process conditions. TCS is separated from them, and the other chlorosilanes are further refined to the required purity levels, mainly by fractional distillation. The TCS is then mixed with hydrogen and decomposed in the Siemens reactor, yielding solid high-purity silicon and large amounts of silicon tetrachloride (STC, SiCl₄) as a by-product:



Siemens reactors are hot-filament cold wall reactors in which pure silicon rods are heated up through the Joule effect by means of an electrical power supply with variable current and voltage. As the silicon deposition

reaction takes place in the surface of the rods, their diameter grows, until it reaches a maximum value that depends on reactor geometry.

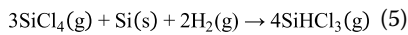
Unreacted TCS and other chlorosilanes present in the Siemens gaseous effluent are condensed and hydrogen is recovered. STC is transformed back to TCS by a high-temperature conversion reaction:



This has been the technology used by incumbent producers for many years, and is still in use by many of them today, their proprietary developments being better than the commercially available alternatives.

b) TCS Siemens with hydrochlorination (HC) (Fig. 2(b))

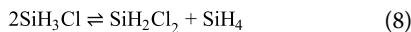
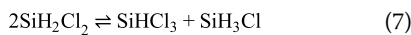
MG-Si and silicon tetrachloride, recovered from the deposition step, react with hydrogen to produce TCS, according to the following overall stoichiometry:



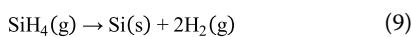
As in the case of the DC process, chlorosilanes are separated and purified by means of a fractional distillation stage. Pure TCS is fed into the Siemens reactor, and STC is recycled to supply the hydrochlorination step. This technology has been adopted by most of the Chinese producers since 2012, following the sharp drop in polysilicon price that came with the oversupply.

c) MS Siemens

Only REC Silicon uses the MS Siemens process on a commercial scale. TCS is synthesized by hydrochlorination (Equation 5) and is subject to redistribution reactions to produce silane along with silicon tetrachloride, which is recycled to supply the hydrochlorination step.



The silane, after being purified, is fed into a Siemens-type reactor. Silane decomposition does not yield any by-product apart from hydrogen, which is normally used as a carrier gas in these reactors.



d) MS FBR (Fig. 2(c))

This alternative, known as the *Union*

Carbide Process, has the same flow diagram as the MS Siemens process, the only difference being that the deposition of solid silicon takes place in an FBR. This reactor has a continuous supply of silane and small beads of pure silicon, which are the seeds for heterogeneous deposition of silicon. Only REC Silicon uses this technology on a commercial scale, although GCL-poly has recently started pilot production. In the case of SunEdison, its plant in Pasadena, Texas, uses an alternative process for silane production, known as the *ethyl corporation process*, in which an alkaline fluorosilicate serves as the starting material instead of MG-Si.

e) Other chemical processes

Many processes have been studied and scaled up with different degrees of success. The most important is CVD in the FBR from trichlorosilane, which can be obtained by the procedures described for Siemens technology. Several plants on a pilot scale have been operated by various companies, but their maturity has not yet been sufficiently proved for them to be scaled up to commercial throughputs.

“Many processes have been studied and scaled up with different degrees of success.”

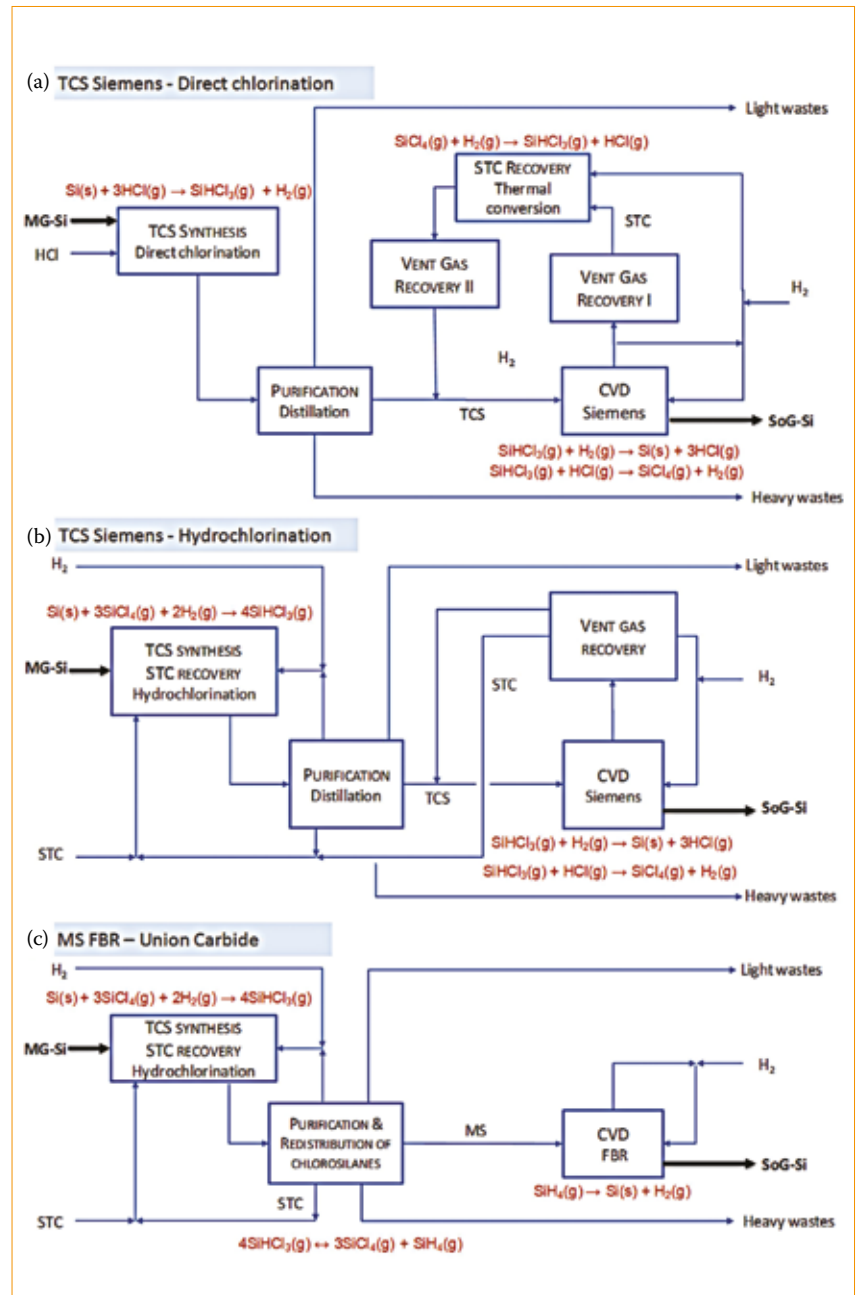


Figure 2. Simplified block diagrams of polysilicon production: (a) TCS Siemens with direct chlorination; (b) TCS Siemens with hydrochlorination; and (c) MS FBR (with hydrochlorination and redistribution).

Of the above-mentioned technologies, two are used industrially for polysilicon production by chemical methods. The first is traditional trichlorosilane Siemens-based silicon deposition, which accounts for around 90% of the total polysilicon production, both by direct chlorination and by hydrochlorination. The second is FBR deposition from silane, responsible for the other 10% of polysilicon production.

Quality

The global industry association of micro- and nanoelectronics, which includes the PV industry, has issued a standardized specification to classify the different categories of silicon for PV applications [26], that is to say, SoG-Si (see Table 1, in which the values in ppm_w have also been included, along with the total purity in nines N). This classification includes silicon feedstock purified by the metallurgical route (grades III, IV), as well as polysilicon for PV applications (grades I, II).

The standardization of SoG-Si, however, is not straightforward, since the elements present in the silicon feedstock have different effects on cell performance. For standardization purposes, three different categories of element within silicon can be defined: dopants (B, P, Al, etc.), metallic impurities (Fe, Cr, Ni, Ti, etc.) and non-metal impurities (N, O, C, etc.).

“The elements present in the silicon feedstock have different effects on cell performance.”

The type of silicon (n or p) is defined by the concentration of dopants (donor or acceptor). In the case of SoG-Si, the material is usually compensated with a significant concentration of donors and acceptors. The compensation ratio $R_c = (N_A + N_D) / |N_A - N_D|$ is a figure of merit that involves the level of compensation and the total concentration of dopants.

Dopants

Boron is an acceptor p-type dopant. It has similar properties to silicon, which makes it a difficult element to remove from silicon and its compounds. The SoG-Si producer has to balance the concentration of B in the silicon and the resources needed to reduce its concentration to an acceptable limit. This is also true for P, a donor dopant responsible for the n-type characteristic of silicon. As can be expected from this consideration, the compensation of silicon and its influence on final cell performance have been studied from the point of view of minority-carrier lifetime and mobility [27]. It has been reported that the reduction of minority-carrier mobility because of scattering

in ionized impurities is balanced by the increase in lifetime as a result of free-carrier reduction [28]. Other authors have described a net improvement in solar cell performance when using compensated silicon [29], but this is in contradiction to the results obtained by Hoffmann et al. [30], who showed a linear decrease in efficiency with R_c in solar cells made of UMG feedstock. Other considerations as well as mobility and lifetime therefore have to be taken into account:

- Compensated silicon presents a low yield in silicon growth. The reason for this is that the high concentration of P tends to change the resistivity of the ingot from positive (in the case of p type) to negative as a result of the accumulation of P in the melt in the final stages of silicon growth. This effect can be mitigated by doping the charge with gallium [31].
- It is known that boron in combination with oxygen has an effect on light-induced degradation (LID). For p-type solar cells made of polysilicon, an LID of 0.5 to 1% has been shown for Cz-Si solar cells, whereas for multicrystalline solar cells the LID has been found to be lower – 0.1 to 0.2%_{abs} [32]. However, for solar cells made of UMG, an LID of up to 2.5%_{abs} has been reported [33].
- Dopant atoms can themselves form recombination-active centres, such as

	Grade I		Grade II		Grade III		Grade IV	
	ppb _a	ppm _w	ppb _a	ppm _w	ppb _a	ppm _w	ppb _a	ppm _w
B	1	0.00038	20	0.01	300	0.12	1000	0.38
C	300	0.12828	2000	0.86	5000	2.14	100000	42.76
Na	10	0.00819	50	0.04	100	0.08	4000	3.27
Al	1	0.00096	20	0.02	300	0.29	1000	0.96
P	1	0.00110	20	0.02	50	0.06	720	0.79
K	10	0.01392	50	0.07	100	0.14	4000	5.57
Ca	10	0.01427	50	0.07	100	0.14	4000	5.71
Ti	10	0.01705	50	0.09	100	0.17	200	0.34
Cr	10	0.01851	50	0.09	100	0.19	200	0.37
Fe	10	0.01989	50	0.10	100	0.20	200	0.40
Ni	10	0.02090	50	0.10	100	0.21	200	0.42
Cu	10	0.02263	50	0.11	100	0.23	200	0.45
Zn	10	0.02328	50	0.12	100	0.23	200	0.47
As	1	0.00267	20	0.05	50	0.13	720	1.92
Mo	10	0.03416	50	0.17	100	0.34	200	0.68
Sb	1	0.00433	20	0.09	50	0.22	720	3.12
	6.7N		5.8N		5.5N		4.3N	

Table 1. SEMI classification of silicon for PV applications [25].

the already mentioned boron–oxygen defect or FeB and CrB [27].

- Although compensation can enhance cell performance because of the increase in carrier lifetime, this applies to already compensated silicon, which has a high concentration of B and P as well as other doping species [29], and should not lead to the conclusion that compensated silicon is better than high-purity silicon. Taking into account ingot yield, LID and cell efficiency, Degoullange et al. [33] suggest the following specifications for UMG-Si:

$$[B] < 0.2\text{ppm}_w, [O_i] < 20\text{ppm}_w \text{ and } [P] < 0.5\text{ppm}_w$$

whereas Hoffmann et al. [30], according to the limiting influence of dopant concentration on solar cell efficiency, propose:

$$[B] < 0.15\text{ppm}_w \text{ and } [P] < 0.3\text{ppm}_w$$

Metallic impurities

Metallic impurities introduce deep energy levels in the silicon band gap that act as minority-carrier recombination

centres, provoking a decrease in solar cell performance. Moreover, it is known that interstitial Fe forms pairs with B; this introduces, within the gap, energy levels close to the conduction band, thus reducing the minority-carrier lifetime [34]. The same happens with Cr atoms, but this new energy level is close to the valence band [29]. Metals such as Fe and Ni can form precipitates that also act as recombination centres [34–36].

The impact of some metallic impurities can be reduced by techniques such as gettering [34,37,38] or hydrogenation [39], performed at the solar cell production level. Regarding their behaviour and influence within the solar cell, metal impurities can be divided into two categories: fast-diffusing impurities (e.g. Fe, Cr, Cu and Ni), which are receptive to gettering, and slow diffusers (e.g. Ti, Mo and V) [40]. The latter should be avoided, as they have a significant negative impact on solar cell efficiency because of their insensitiveness to gettering.

Aluminium is also a critical element, since it is an acceptor like boron. As a

consequence, the resistivity and carrier concentration are strongly affected by this metal impurity; moreover, it cannot be reduced by gettering. Owing to the features of the Silicor process, aluminium is an element that can be found at high concentrations in this company's product. According to studies related to Silicor UMG [38], the performance of cells made of compensated silicon that were intentionally contaminated with Al up to 1ppm_w showed a $3\%_{\text{rel}}$ lower efficiency than those without that extra contamination. Aluminium in silicon can also originate from the alumina insulators of directional solidification furnaces as well as from some furnaces used in UMG processes.

Non-metallic impurities

Non-metallic impurities consist mainly of C, N and O. The sources of these elements are diverse: for example, carbon can be incorporated into the silicon during its growth, as some of the thermal insulators of furnaces are made of graphite. This is also the case in the

	Siemens						FBR	UMG			Other
	Producers A and B Specs – Low Grade	Producers A and B Specs – High Grade	Producer C Specs – High grade	Producer D Specs – Solar poly	Producer E Specs – Solar poly	Producer F Specs – Solar poly	Producer G Specs – Granular poly	ELKEM Specs – ESS 2015 [46]	Silicor Materials Promotional data 2015	PHOTOSIL Published data 2015 [18]	RSI Promotional data 2015
B	1	0.2	0.04	0.04	0.04	1.92	0.31	200	300	300	81
P	8.5	1.65	0.44	5.51	0.33	5.51	0.88	600	740	600	84
Al						10		150	100	100	18
Ti								80			
Cr				2	1	2					12
Fe				10	10	10		80		100	80
Ni				2	1	2					20
Cu				2	1	2				100	30
Zn				4	2	4					5
Na				15	6	15			50		26
K				10		10					15
Ca								3000			50
Bulk metals (Fe,Cu,Ni,Cr,Zn,Na)			3	15	2	15					
Surface metals total			5	30			30*				
Oxygen	1710	1140									
C	385	214	43	43	107	428	100		15		

*ppb_a

Table 2. Concentrations of impurities (ppb_w) for different SoG-Si producers. All data are extracted from specifications, promotional data or publications, and are therefore maximum values. (Empty cells represent no available data.)

metallurgical purification of silicon, which also uses graphite crucibles to perform the silicon casting. In silicon growth, nitrogen is also incorporated from the Si_3N_4 coating of the crucibles used in the directional solidification of multi-crystal ingot growth. During Czochralski growth for producing single-crystal ingots, the contamination of silicon with oxygen coming from the silica crucible is also very common.

As a result, the concentration of C, N and O in silicon is about one order of magnitude greater than that of metals. Carbon and nitrogen can form precipitates of SiC and Si_3N_4 during silicon solidification. Those precipitates are very harmful, as they provoke lattice distortions, shunts in solar cells [41], wire breakage during ingot wafering, crucible damage during MG-Si purification, and so on. In particular, carbon is very detrimental to Czochralski (Cz) growth; silicon for that purpose therefore typically has a C concentration below 1ppm_w , which makes UMG-Si unsuitable for direct use in single-crystal wafers. Directional solidification for multi-crystal ingot growth, on the other hand, permits up to 30ppm_w of carbon [4].

The relationship of oxygen, in combination with boron, to LID was mentioned earlier. For granular silicon obtained by FBR deposition, the silicon oxide formed on the surface of the silicon grains as soon as they are exposed to air is very extensive because of the high surface-to-volume ratio. Moreover, during the CVD process, hydrogen is absorbed on the surface of the particles, which can

cause explosions and the splashing of molten silicon during ingot growth. Siemens polysilicon, however, does not exhibit this high O concentration, as it is obtained as large chunks. Graphite pieces are also used in Siemens-type CVD reactors, although the silicon in contact with these pieces is separated from the rods and sold separately as a different grade of polysilicon.

A comparison of the main impurity concentrations for different SoG-Si, including polysilicon, extracted from specification sheets available online and documentation made public by producers, is shown in Table 2. Several studies on the efficiency of solar cells fabricated from UMG-Si [30,38,42–44] or from intentionally contaminated silicon [45] have been conducted; the resulting efficiencies are quite similar to those obtained from polysilicon feedstock, and the outdoor power degradation is low [46].

In Fig. 3 the concentration ranges of boron and phosphorus for different commercial products are compared and classified according to the standard specifications for the four defined grades.

Technological challenges of reducing cost

Chemical route

Although the application of TCS Siemens technology to the industrial production of polysilicon dates back to the 1960s, it is only during the last decade, driven by the pressure of the PV market, that a significant cost reduction has been achieved by process optimization. In this regard,

the replacement of inefficiently designed or nonexistent STC recovery schemes by the proven more cost-effective hydrochlorination technology has put some of the new producers, especially in China, in a position to realise cash operation costs below $\$12/\text{kg}$ [4].

A large part of the cost reduction has been achieved in Siemens deposition reactors. The development of both equipment and recipes that are tailored to solar-grade polysilicon production, and are less demanding in terms of purity than electronic-grade polysilicon, has led to higher silicon deposition velocities and throughput, resulting in lower costs. Energy-saving strategies, mainly the reduction of heat losses and the recovery of part of the supplied electrical power as vapour for heating in other processes of the polysilicon plant (such as the fractional distillation of chlorosilanes), have reduced specific electricity consumption to around $45\text{kWh}/\text{kg}$ for state-of-the-art Siemens reactors; of this, over 50% can be recovered.

“The main strength of silane deposition in FBRs is the very low energy demand of these reactors.”

On the other hand, the main strength of silane deposition in FBRs is the very low energy demand of these reactors – as low as $5\text{kWh}/\text{kg}$. The low-cost mass production of granular polysilicon is currently taking shape. Two joint ventures have been established by the companies with industrial experience in FBR deposition – SunEdison and REC Silicon – with new plants also employing this technology. In addition, GCL-poly has become a new player in FBR technology, setting up a plant that started its ramp-up in 2014 [25]. Centrotherm SiTec, one of the top polysilicon technology providers, has recently announced that it is developing its own FBR CVD process and reactors [48], which are expected to be available within two years.

Even though at first sight the large difference that exists between electrical power consumptions might suggest that traditional Siemens reactors should be replaced by FBR technology, other important aspects need to be taken into account, such as the quality of the product [49]. Further progress is expected for both technologies.

Although major improvements in

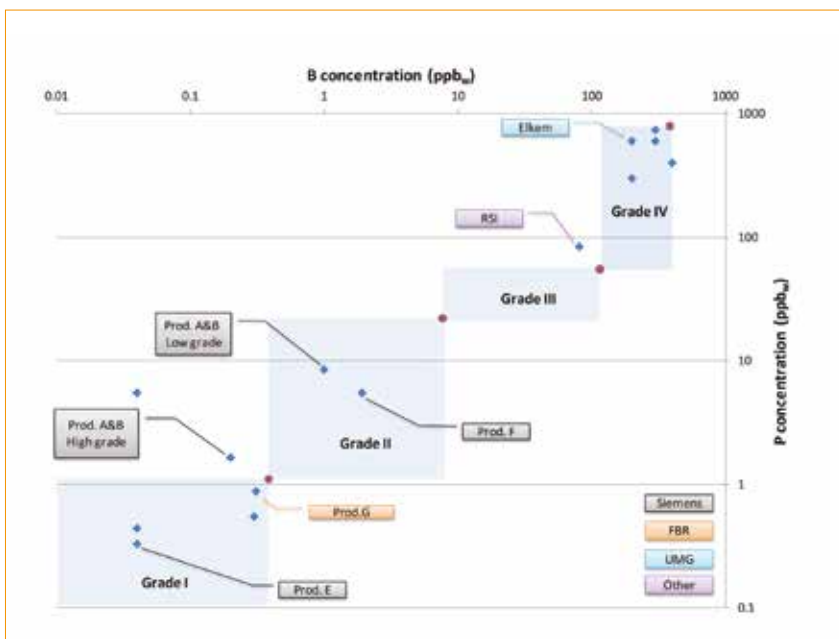


Figure 3. Concentration ranges of boron and phosphorus in different SoG-Si specifications.

performance and costs have been achieved during the last decade, research and development is still being carried out regarding the deposition equipment and processes, including studies of CVD in FBRs, for both silane and trichlorosilane [50,51], and of the energy consumption reduction of Siemens reactors.

The precursor synthesis, to produce TCS and MS, has a lower impact on overall polysilicon production costs. Hydrochlorination, because of the advantages of combining TCS synthesis and STC–TCS conversion in one step, has been replacing a significant part of the direct chlorination and thermal conversion capacity during the last few years. While hydrochlorination has advantages over the direct chlorination and thermal conversion combination, it also has some drawbacks, such as the low STC conversion rate and the need to combine pure and impure streams, which result in the need to manage a greater amount of material, especially recycled STC. New reactions are being studied, such as the catalytic hydrodechlorination of STC [52], in order to avoid the introduction of additional impurities into the TCS synthesis, and thus reduce costs associated with purification.

Metallurgical route

Unlike the chemical route, the metallurgical route emerged with the clear aim of reducing the costs of producing SoG-Si, which means the margin for further cost reduction is much 'thinner'. The main challenges of the metallurgical route are the reduction of silicon losses and the recycling of intermediate silicon to obtain satisfactorily refined silicon. Some of the metallurgical processes (described above) are based on the accumulation of impurities in certain small segments of the silicon. Those

parts are rejected (which accounts for silicon losses) or recycled, thus increasing the production costs.

Most of the metallurgical treatments are followed by a block casting in which some kind of directional solidification is performed. The environment during that solidification, the mass transport to the solidification front, and the material of the crucibles or moulds are essential factors that directly influence the yield of purified silicon. As in directional solidification, the purification by vacuum or gas treatment requires a stirring of the silicon melt in order to increase the mass transfer of impurities to the surface, where the refining takes place.

In acid leaching, the optimal size of silicon chunks is of major importance in optimizing the removal of impurities from the grain boundaries and the surface. In this case, the waste treatment of by-products is very important. For slag treatment, it is essential to choose

the correct slags, as well as the contact optimization between slags and silicon. Key steps after the refining are the complete extraction of slags from the melt and their post-processing, as these can contain a high percentage of usable silicon.

In summary, effective processes in terms of silicon yield and reduction of losses are critical in achieving low operational cash costs and energy consumption. The authors consider that, for metallurgical purification, the operational cash costs should be below \$12/kg and the energy consumption below 25kWh/kg, although other considerations, such as capital expenditure, are important.

Cost analysis

Some studies have been published in the past regarding polysilicon production costs [53–55], but there is a lack of information about the costs of

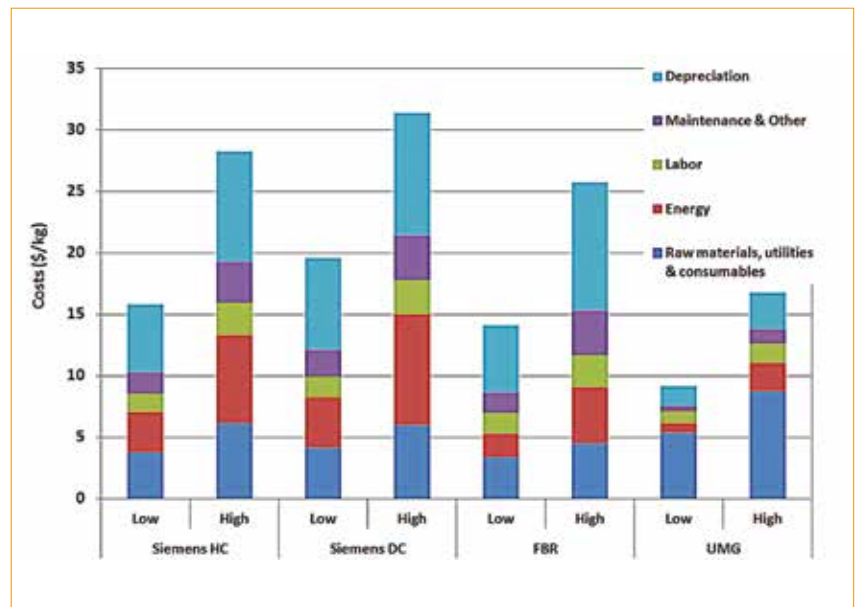


Figure 4. Cost breakdown for different technologies for state-of-the-art facilities and low- and high-cost scenarios.

	Siemens HC		Siemens DC		FBR		UMG	
	Low	High	Low	High	Low	High	Low	High
Raw materials, utilities and consumables	3.8	6.1	4.1	6.0	3.4	4.5	5.4	8.8
Energy	3.2	7.2	4.1	9.0	1.9	4.5	0.8	2.3
Labour	1.5	2.6	1.7	2.8	1.7	2.6	1.0	1.6
Maintenance and other	1.8	3.3	2.2	3.6	1.7	3.6	0.4	1.1
Cash cost	10.3	19.2	12.1	21.4	8.6	15.3	7.5	13.8
Depreciation	5.5	9.0	7.5	10.0	5.5	10.5	1.6	3.0
Manufacturing cost	15.8	28.2	19.6	31.4	14.1	25.8	9.1	16.8

Table 3. Cost breakdown [\$/kg] for different technologies for the best state-of-the-art facilities and low and high scenarios.

the main silicon-refining technologies, namely Siemens, FBR and UMG. Cash costs can be analysed for these cases by taking into account various requirements, such as raw materials, utilities, energy, labour, consumables and maintenance.

It is important to note that there are other aspects, apart from the technology itself, which have a significant impact on the final cash cost figure – electricity price and labour wages at the location of the facility, MG-Si and other raw material prices, the level of automation and scope of the facility (for example, whether or not it manufactures some of the raw materials in-house), and so on. The proposed breakdown, which is useful for comparing different technologies, evaluates a low- and a high-cost scenario for each technology, taking into account appropriate ranges of values for both consumption and unitary cost.

The calculation of the costs is based on the assumption of a nominal capacity of over 15,000MT/year with the use of state-of-the-art technology. The data are presented in Table 3 and shown graphically in Fig. 4. Auxiliary chemicals or waste treatment are included under the category of ‘other’.

The manufacturing costs for polysilicon depend on the specific technology. In the case of the chemical route, Siemens with hydrochlorination and FBR can yield costs below \$20/kg. For UMG-Si production, the manufacturing costs can come to just under \$10/kg in a low-cost scenario, characterized by much lower capital costs (around one-third) when compared with the rest of the processes.

Conclusions

This paper has reviewed the key technological quality vs. cost aspects associated with the chemical and metallurgical approaches to silicon refining. The representative techniques of silicon purification used in both of those approaches have been briefly described. The study of quality, although applicable to any type of silicon, has focused on the metallurgical route because the obtainable purity is lower than that for the chemical route; indeed, a comparison of the concentration of different elements in SoG-Si materials showed a lower presence of impurities and dopants in the silicon obtained by chemical processes. The key question, then, is what the level of purification needs to be achieved in order to strike a good balance between costs and potential cell efficiency.

“UMG-Si can be considered to be a good alternative to polysilicon.”

Studies referenced in the ‘Quality’ section, and work carried out by Aurinka, reveal that the solar cell efficiencies obtained from UMG feedstock are close to those obtained from polysilicon, leading to the conclusion that UMG-Si can be considered to be a good alternative to polysilicon. Cell production treatments (gettering, hydrogenation, etc.) that focus on the minimization of the effects of contaminants can offer positive contributions, with further increases in cell efficiency. Finally, the production cash costs of UMG-Si and FBR compared with Siemens HC and Siemens DC make the former alternatives a reasonable choice, especially taking into account that silicon feedstock prices fell to \$14/kg, or even lower, towards the end of 2015 [1,56].

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