

Silicon processing: from quartz to crystalline silicon solar cells

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Abstract – Silicon has been the dominant material in the photovoltaic (PV) industry since its application in the space industry in 1958. This review focuses on crystalline silicon solar cells, primarily due to their dominance in the photovoltaic industry, omitting other photovoltaic cell technologies such as second generation (*e.g.* thin films) and third generation (*e.g.* nano-structured solar cells).

The value chain for the production of crystalline silicon solar cells has been reviewed. The primary processing steps for the production of silicon solar cells from quartz are as follows: bulk production of metallurgical-grade silicon via carbothermic reduction in a submerged furnace, refining of metallurgical-grade silicon via the chemical means to polycrystalline silicon, or through the metallurgical route to solar-grade silicon, wafer manufacturing, and, lastly, silicon solar cell manufacturing. During downstream processing, solar cells are interconnected and encapsulated into solar modules (panels), which can be used individually or incorporated into a photovoltaic system for electricity generation and supply. The cost for crystalline silicon based solar cells is approaching one US dollar per watt peak (\$1/W_p), while the most cost-effective solar modules in industry have reported costs below \$1/W_p, and are based on CdTe thin films. Solar cell energy conversion efficiencies as high as 22% have been reported in industry for crystalline silicon solar cells.

INTRODUCTION

The unsustainable nature of fossil fuels as an energy source, from the point of view of future availability and environmental impact, has spurred an interest in diversification of energy sources, with particular interest in renewable energy. The photovoltaic (PV) industry is a player in the renewable energy segment, and the electricity generation from photovoltaics (solar cells) is deemed to be one of the key technologies of the 21st century.¹ Photovoltaic solar electricity presents an elegant means for electricity generation, as there are no moving parts, zero emissions, and no noise.

The photovoltaic industry is booming, growing at double-digit growth rates per annum², and is anticipated to maintain this boom for years to come^{3,4}. The dominant material used in PV cells is silicon, particularly multi-crystalline silicon⁵. The multi-crystalline silicon market share for PV applications accounted for nearly half of the total PV materials in 2009⁶. Its preference over mono-crystalline silicon is due to lower production costs while maintaining relatively high energy conversion efficiency as a solar cell. The dominance of

the crystalline silicon can be attributed to the maturity of the technology, and lower direct production costs, with a potential for further reduction in costs compared to other photovoltaic technologies⁷. Crystalline silicon is expected to maintain its lead in the near future^{8,9}. A brief history of the origins of modern solar cells is given, and silicon's position in relation to other materials as a solar cell material is evaluated.

Until 1997, the silicon used in the production of solar cells was sourced from waste materials from the electronic industry¹. Subsequently, this became unsustainable due to a mismatch in supply-demand of silicon between the PV industry and the electronic industry, and the costs associated with production.¹ Moreover, the chemical purity requirements of electronic-grade silicon are much more stringent than those of solar-grade silicon. Consequently, technologies for a new silicon feedstock, the solar-grade silicon, tailored for the PV market had to be developed. Two main routes have been developed, or are currently under development, exclusively for the industrial production of silicon for the PV industry, and these are the chemical route and the metallurgical route¹. An appraisal of these processing routes is given in this paper.

The precursor material for both electronic-grade silicon and solar-grade silicon is metallurgical-grade silicon. Once solar-grade silicon is produced, the subsequent processing steps are as follows: wafer production, solar cells manufacture. A short description of these processing steps will be given in the paper. Solar cells are assembled into solar modules for electricity generation. The flowsheets for the production of silicon solar cells from quartz via both the chemical route and the metallurgical route are shown in Figure 1.

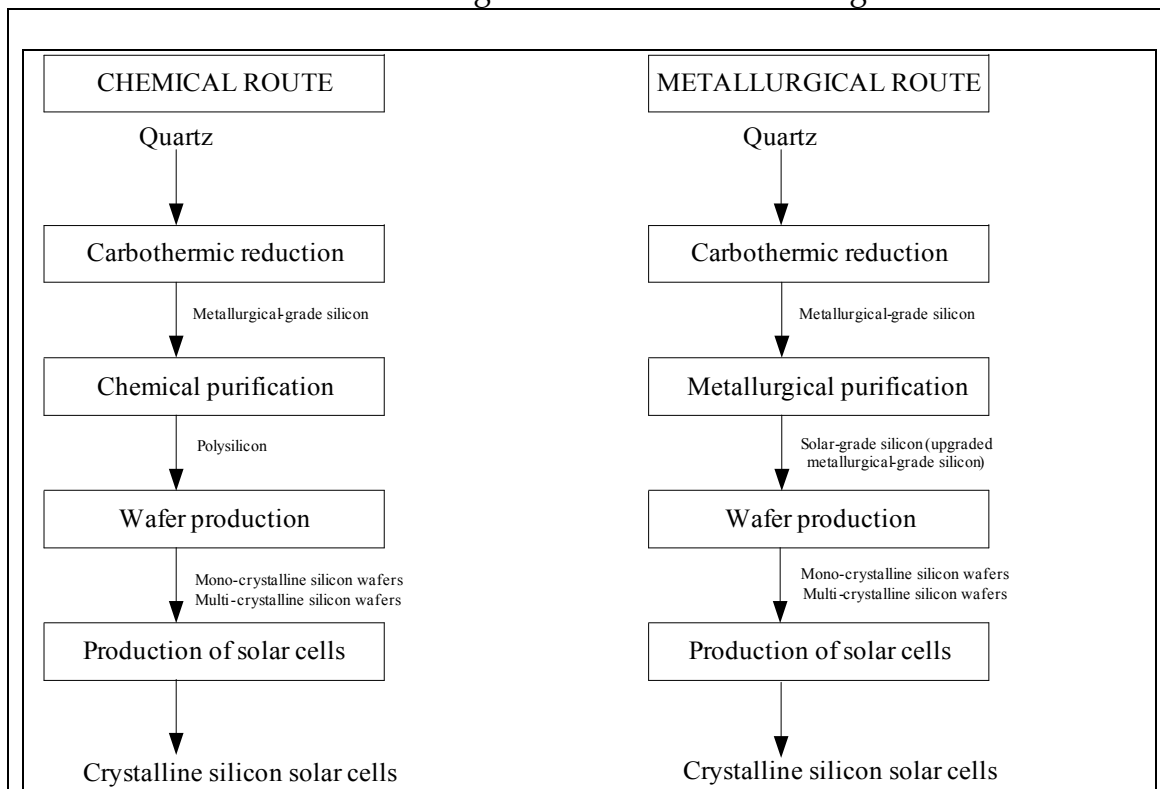


Figure 1: Stages for the production of crystalline silicon solar cells from quartz

ORIGIN OF SILICON SOLAR CELLS

Solar cells generate electricity as a result of the photovoltaic effect. It was not until 1839 that the photovoltaic effect was reported for the first time by Alexandre-Edmund Becquerel, who observed that electrical currents were generated from light-dependence on a silver-coated platinum electrode immersed in an electrolyte¹⁰. A similar effect was observed in an entirely solid-state system in 1876, comprising a selenium sample and platinum contacts.

The first modern silicon solar cell was developed at Bell Laboratories in 1954 by Chapin, Fuller, and Pearson, and had an energy conversion efficiency of 6%¹¹. In the same year, a cadmium sulphide thin-film solar cell was produced and had an energy conversion efficiency of the same order of magnitude as the silicon solar cell¹¹. These efficiencies were remarkable, as solar cells developed up to this point showed energy conversion efficiencies between 0.1% and 0.5%. In 1956, gallium arsenide (GaAs) solar cells with energy conversion efficiency of 6% were reported from Radio Corporation of America (RCA). By 1956, silicon solar cells showed efficiencies as high as 10%. It is reported that the first indium phosphide (InP) and CdTe solar cells were made at RCA, and the best efficiency of these cells was reported as approximately 2% in 1959.

The first major application of solar cells was in 1958, when the USA launched the first satellite using a PV power supply. Silicon solar cells were used for this mission, and up until today silicon solar cells remain the most dominant in the photovoltaic market. Silicon solar cell technology benefited greatly from the silicon technology developed for the electronic industry⁸.

IS SILICON THE IDEAL SOLAR CELL MATERIAL?

As the focus of this paper is on silicon in solar cells, and the basis for electricity generation is the photovoltaic effect, an important question to answer is whether silicon is the ideal solar cell material or not. To answer this question, it is important to consider the relevant chemical, physical, and electrical properties of silicon.

First and foremost, silicon is an indirect band gap semiconductor. Therefore, on the energy-crystal momentum plot, the minimum energy in the conduction band and the maximum energy in the valence band occur at different values of crystal momentum. Consequently, the probability of light being absorbed is much lower than in the direct band gap¹⁸. Light can pass a reasonable distance into the indirect band gap semiconductor prior to absorption. This has adverse consequences when considering the amount of material used; only 1 micron of GaAs (a direct band gap semiconductor) is needed to absorb an equivalent light that is absorbed by 100 microns of silicon⁸.

The solar cell energy conversion efficiency limits, as a function of the band gap of the semiconductor material, can also be used to benchmark silicon against other semiconductor material (see Figure 2).

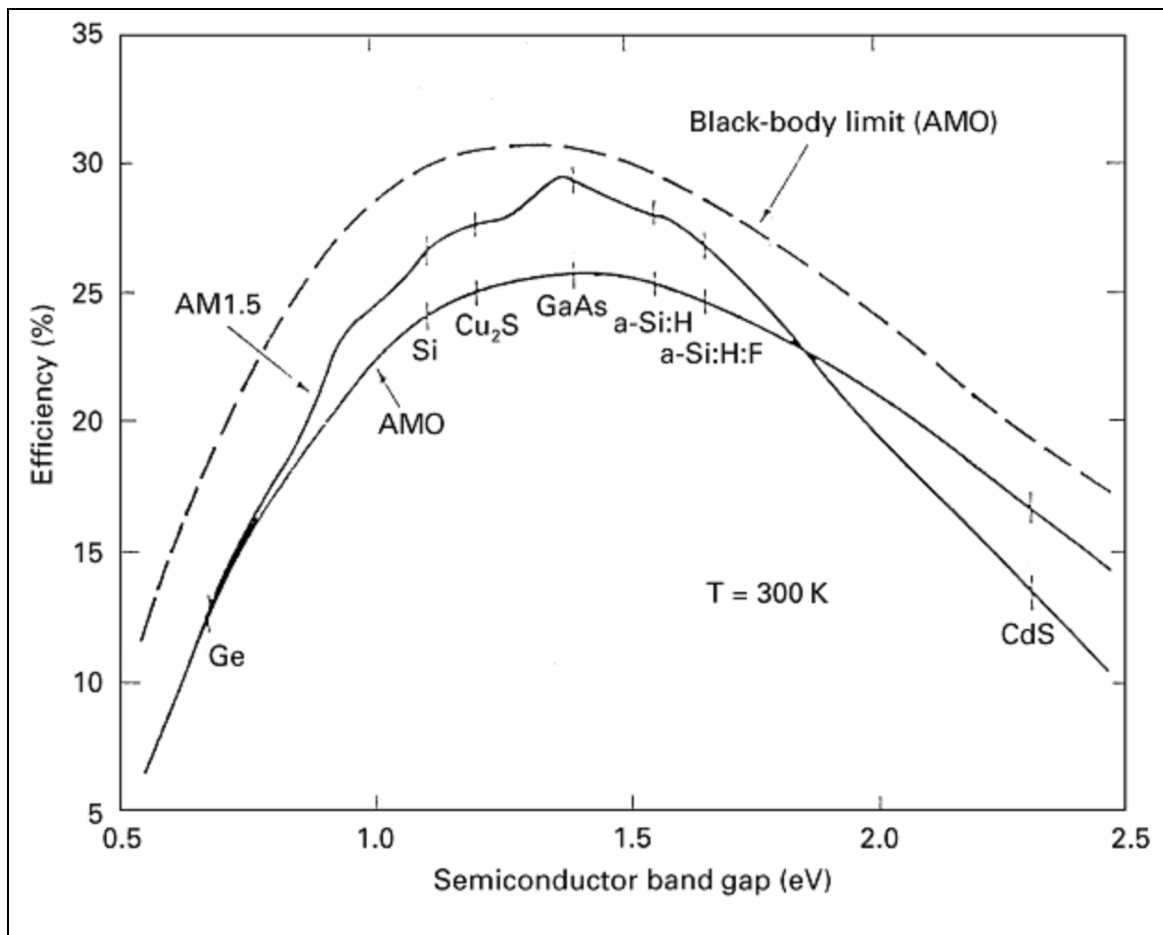


Figure 2: Solar cell energy conversion efficiency limits, as a function of the band gap of the semiconductor material, at different radiation¹²

The solar cell energy conversion efficiency limits shown in Figure 2 are at the following radiations: air mass zero (AM0), air mass 1.5 (AM1.5), and for a black body under air mass zero (AM0). It is known that each photon absorbed by a semiconductor material creates one electron-hole pair regardless of its energy. Moreover, only photons with energy greater than or equal to the band gap of a semiconductor are absorbed by that semiconductor. Therefore, the plot of efficiency as a function of semiconductor band gap has a maximum energy conversion efficiency. As can be seen from the figure, silicon's band gap is below the maximum, which is between 1.4 and 1.6 electron volt (eV).

It is clear from its properties that silicon is not the ideal material for solar energy conversion. It is no surprise that there is extensive research going into the search for new materials for solar cells. Thin-film semiconductors are gaining popularity in industry, particularly cadmium telluride (CdTe), which is only second to crystalline silicon in terms of market share in the photovoltaic industry. Cadmium telluride is both a direct band gap semiconductor and has a band gap within the optimum band gap.

There are other important factors to be considered for an ideal solar cell material; these include: material availability, non-toxic materials, easy production methods suitable for mass production, sound photovoltaic conversion efficiency, and long term stability of the solar cell material¹². As

mentioned previously, the dominance of silicon in the photovoltaic industry is attributed to historic reasons, *i.e.* availability of high-quality material in large quantities for the semiconductor market¹².

FROM QUARTZ TO METALLURGICAL-GRADE SILICON

Silicon is the second most abundant element in the earth's crust, second only to oxygen. It is naturally found as fairly pure silicon dioxide and as silicates. The silicon dioxide is found as huge deposits of quartzite or quartz sand. Moreover, many rocks contain quartz crystals. Therefore, it can be concluded that the resources of silicon are virtually unlimited (although purity varies considerably).

The main applications of silicon are as follows: deoxidation and alloying of steel and cast iron, alloying of aluminium, raw material in the chemical industry, and raw material in the semiconductor industry (electronic devices and photovoltaic cells). A fair share of the silicon produced industrially is in the form of ferrosilicon, while the rest is as metallurgical-grade silicon. Metallurgical-grade silicon is the precursor for polycrystalline or solar-grade silicon used in the photovoltaic industry.

Industrial production of metallurgical-grade silicon

Silicon is produced industrially by carbothermic reduction of silicon dioxide in submerged-arc electric furnaces. Feed materials include a silicon source such as quartz, and a typical reductant blend comprising coke, coal, charcoal, and wood chips. Feed materials are impure, and impurities are carried to a certain extent to the silicon product stream.

A typical industrial silicon furnace has a shell diameter of about 10 m. Three pre-baked carbon electrodes, submerged into the charge materials, supply a three-phase current that heats the charge materials up to about 2 000°C. At this temperature, silicon dioxide is reduced to molten silicon. The furnaces are operated such that there is a layer of solid material (outer reaction zone) on top of the molten bath (inner reaction zone) to maximize the silicon yield. The silicon is tapped from the furnace through a tap-hole at the bottom, and refined by slag treatment or gas purging. During refining, inclusions are removed, and the composition is adjusted to the specified value. Subsequent to refining, the molten alloy is allowed to cool in a mould, and then crushed to a specific size. Metallurgical-grade silicon has a typical specification of 98.5–99.5% for Si¹³. Typical impurities in metallurgical-grade silicon include carbon, alkali-earth and transition metals, as well as boron and phosphorus¹⁴.

A by-product of the silicon smelting process is condensed silica fume. A silicon furnace produces about 0.2 to 0.4 tons of condensed silica fume per ton of silicon metal. The fume reports to the filter plant where it is collected. Condensed silica fume has found a wide array of applications in industry. Figure 3 shows a typical industrial silicon furnace.

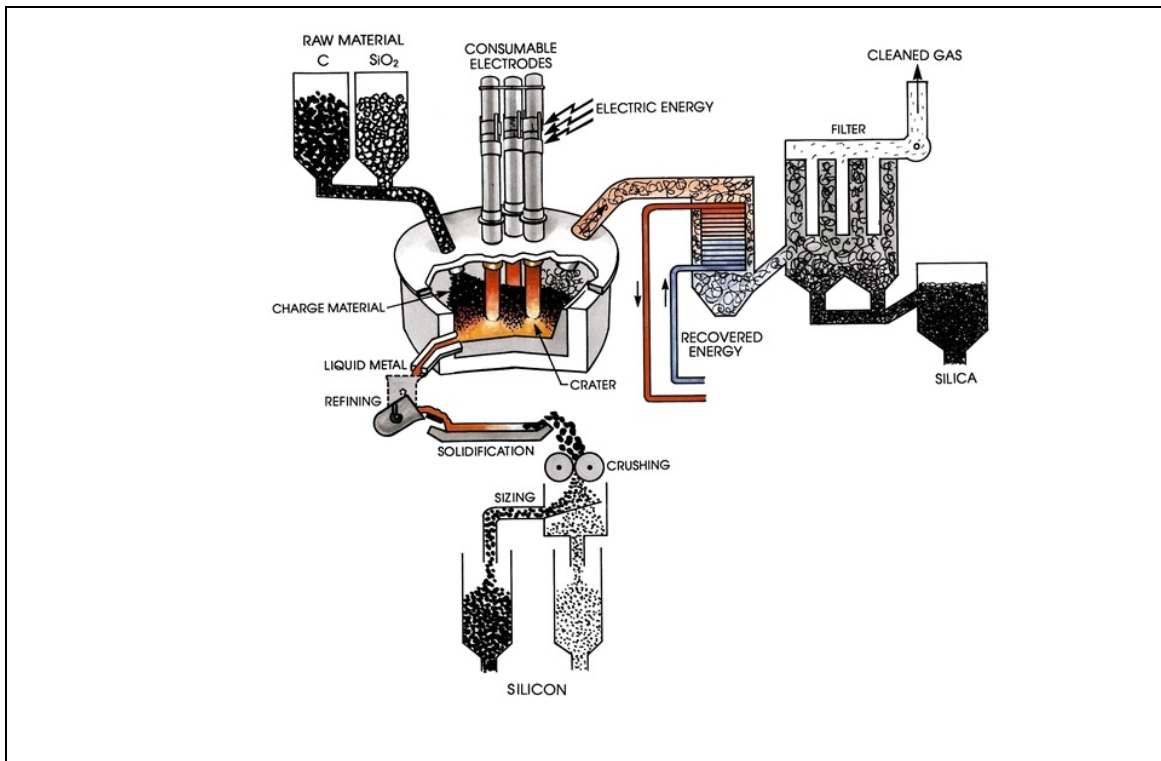


Figure 3: Typical plant layout: industrial production of silicon metal¹⁵

The electrical energy consumption for the production of metallurgical-grade silicon is 11–13 MWh/ton of silicon metal. The energy consumption per ton of alloy is reduced significantly with increasing iron content in the silicon alloy product. The off-gas from the silicon furnace has an energy content of the same order of magnitude as the electrical energy input to the furnace. The off-gas may be directed into an energy recovery system, and can be used to produce hot water or saturated steam for heating, or superheated steam for electricity generation.

The metallurgical-grade silicon is produced in excess of 1 million metric tons/year at a cost of few US dollars/kg depending on quality, purity, and particle size. Metallurgical-grade silicon is produced in countries with cheap electricity, reductants, and good quartz deposits¹³. Demand for metallurgical-grade silicon is primarily from the aluminium and chemical industries, and a small fraction is refined into semiconductor-grade silicon¹. However, this picture is expected to change in the future, as the fastest growing market for silicon metal is the photovoltaic market, with projected consumption exceeding current silicon for all other applications combined by 2020¹⁶.

REFINING OF METALLURGICAL-GRADE SILICON TO SOLAR-GRADE SILICON

Impurities play a vital role in silicon solar cells. Impurities such as boron and phosphorus, in small amounts, are desirable for the formation of the p-n junction that is necessary for electricity generation in the silicon solar cell, while other impurities have adverse effects on solar cells. Impurities can lead to the

formation of defects, and enhance the formation of dislocations, which act as recombination centres of photo-carriers and can compromise both mechanical and electrical properties as well as decrease the solar cell efficiency.^{6,17} Moreover, impurities in solar cells generally introduce allowed levels into the forbidden gap and thereby act as recombination centres, and an increased density of such centres decreases the cell efficiency¹⁸. The effect of metallic impurities on silicon solar cells is shown in Figure 4.

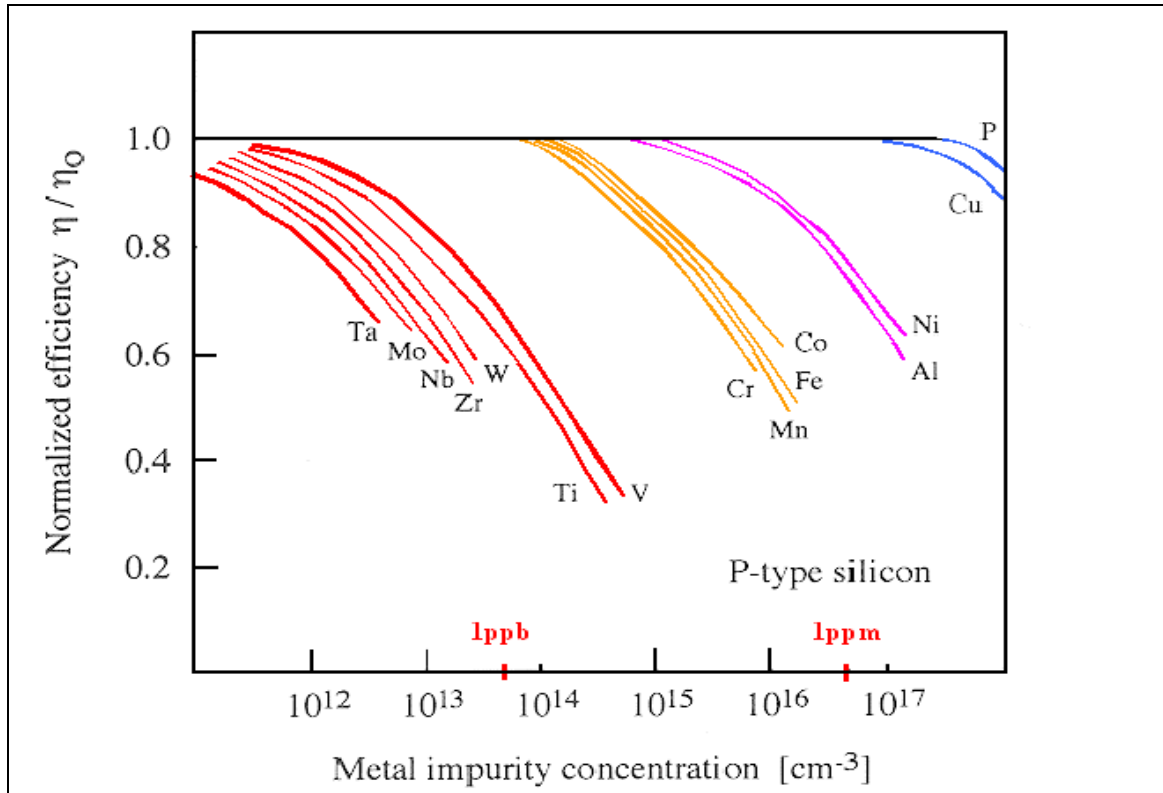


Figure 4: Silicon solar cell performance as a function of secondary impurities in p-type silicon¹⁸

The metal impurity concentration given in Figure 4 is expressed as the number of atoms of impurity per cm^3 . Albeit that some impurities can reduce cell performance when present in extremely low concentrations, others can be tolerated at higher levels. The concentrations of these impurities are much lower compared to impurity concentration found in metallurgical-grade silicon (see Table 1). Therefore, refining of metallurgical-grade silicon is a necessary step¹⁴. However, these impurities are higher than the impurity levels in electronic- (semiconductor-) grade silicon, as shown in Figure 4. It is from this position that potential exists for the production of less expensive and less pure solar-grade silicon, tailored for the photovoltaic market. It must be noted that solar-grade silicon does not have formal specifications; acceptable concentrations of impurities are usually reported instead. The solar-grade silicon analyses reported in Table 1 provide a guideline rather than a specification for solar-grade silicon.

Table I: Typical chemical analyses of silicon products for the semiconductor industry

Element	Metallurgical-grade silicon ¹⁸ (ppm)	Solar-grade silicon ^{7,19} (ppm)	Polycrystalline solar-grade silicon ²¹	Electronic-grade silicon ¹⁹ (ppm)
Si*	99	99.999 9	99.999 99	99.999 999 999
Fe	2 000–3 000	<0.3		<0.01
Al	1500–4 000	<0.1		<0.0008
Ca	500–600	<0.1		<0.003
B	40–80	<0.3		<0.0002
P	20–50	<0.1		<0.0008
C	600	<3		<0.5
O	3000	<10		
Ti	160–200	<0.01		<0.003
Cr	50–200	<0.1		
* Si content in mass %				

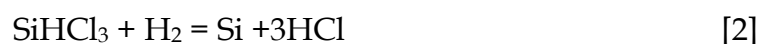
The process for obtaining polycrystalline solar-grade silicon is divided into the chemical route and the metallurgical route, as mentioned previously. These processes will be discussed in detail in the following sections.

Chemical route

The traditional Siemens process is the baseline process for the production of polysilicon. The process was originally developed for the production of electronic-grade silicon in the 1950s. The production scheme is as follows: gasification of metallurgical-grade silicon, distillation, and deposition of ultra-pure silicon. The detailed processing sequence is that fine metallurgical-grade silicon particles are fluidized with hydrochloric acid, in the presence of a catalyst, to produce trichlorosilane according to Reaction 1.



The trichlorosilane liquid undergoes multiple fractional distillation to produce a semiconductor-grade trichlorosilane. The semiconductor-grade trichlorosilane is then reduced by hydrogen in a Siemens reactor, and silicon is deposited in a fine-grained polycrystalline form on an electrically heated inverse U-shape silicon rod ($T > 1100^\circ\text{C}$) in a cooled Siemens reactor¹⁸. The deposition reaction is shown in Equation 2.



The latter step is energy intensive, and has a low yield. The energy consumption of the Siemens process is in excess of 100 kWh/kg Si^{1,15}. A typical Siemens process flowsheet, as described above, is shown in Figure 5.

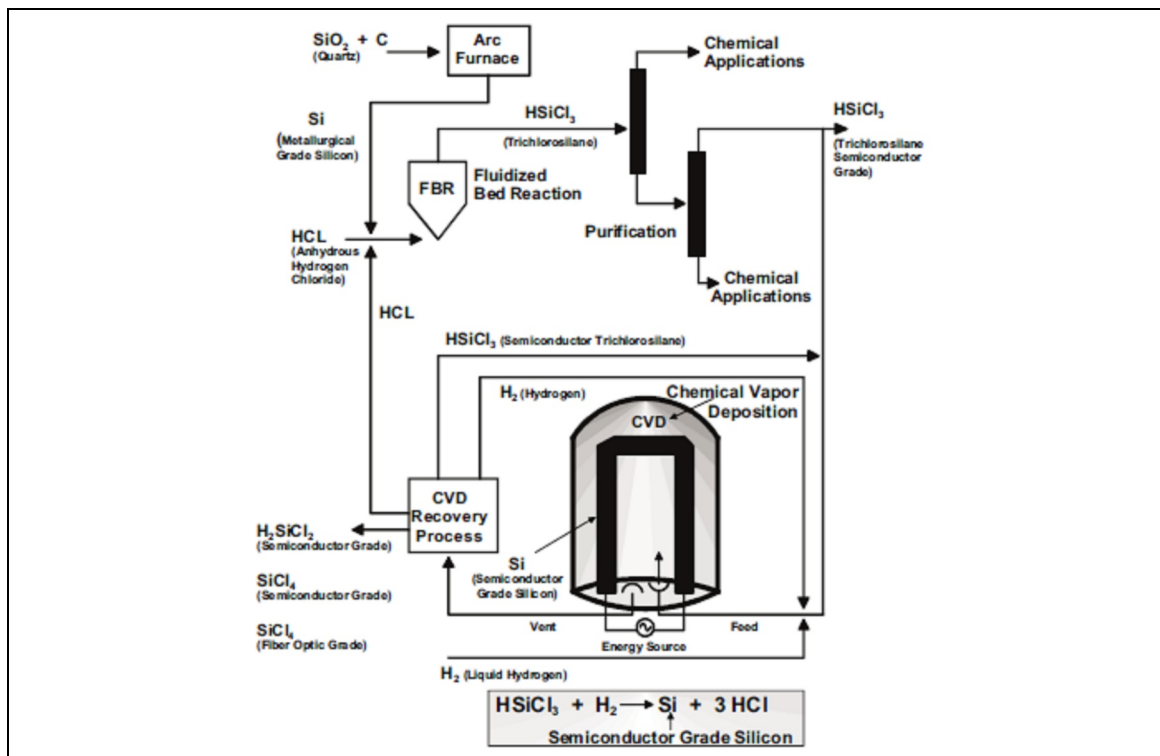


Figure 5: Typical flowsheet for industrial polysilicon production via the Siemens process¹³

There have been advances on the chemical-route technologies targeted at the production of solar-grade silicon. The highly volatile silane (SiH_4) can be used instead of the trichlorosilane during decomposition, and this has advantages over the use of trichlorosilane¹³. One process developed for the production of low-cost solar-grade silicon involves deposition in a fluid bed reactor instead of deposition in the Siemens reactor. The fluid bed reactor is more energy efficient; it produces more silicon per volume of reactor; it is a continuous process rather than a batch process; and, unlike the Siemens process, which requires the breaking of polysilicon rods, the grains produced in the fluidized bed reactor are in a usable form²⁰. The processes mentioned in this section are amongst those that are currently used in industry; there are other emerging chemical processes that have been omitted^{1,13}. The industrial processes discussed above, including the Siemens process, produce polysilicon with a purity of 99.999 99% for both the photovoltaic market and the electronic industry. Polysilicon under relaxed operation can be produced, but such a polycrystalline material would only be suitable for the solar industry. In 2006, the solar industry surpassed the semiconductor industry as the largest consumer of polysilicon²¹. The Siemens process accounted for about 78%, and the fluidized bed reactor for about 16% of polysilicon produced in 2008. The total polysilicon produced in 2008 was approximately 75 000 metric tons, of which 45 000 metric tons was used in the photovoltaic industry²².

Other than the high energy consumption, the major problem with the chemical route is that it involves production of toxic and corrosive compounds; examples include chlorosilanes and hydrochloric acid¹. The developments in the

chemical route are at advanced stages compared to the metallurgical route that will be discussed in the following section.

Metallurgical route

The metallurgical route entails obtaining solar-grade silicon directly from metallurgical-grade silicon via a series of metallurgical refining steps. Solar-grade silicon produced via the metallurgical route is often referred to as upgraded metallurgical-grade silicon. The energy consumption of the metallurgical route is expected to be significantly lower than that of the Siemens process.

Most metallic elements have a low segregation coefficient in silicon, which means that the solid rejects impurities into the liquid during crystallization. The refining techniques based on this principle include both directional solidification and acid leaching. Directional solidification can also be used as a casting step for preparation of single-crystal and multi-crystal ingots from which wafers are prepared. Due to the importance of the casting step, it will be discussed separately.

Other impurities have high segregation coefficients in silicon; these include boron, carbon, oxygen, and phosphorus. Therefore, such impurities cannot be removed from silicon via the above-mentioned refining techniques. Phosphorus can be volatilized from silicon, and removed via vacuum refining. Boron can be removed from silicon by slag refining, or via plasma refining where carbon and oxygen are also removed. It is common in the metallurgical route to employ high-purity raw materials, *i.e.* purified quartz, carbon black, and high-purity electrodes; this renders low impurity levels in the upgraded metallurgical-grade silicon product.

Since the refining techniques used in the metallurgical route tend to be effective in removing specific impurities, combinations of the refining steps are employed in industry for effective refining of metallurgical-grade silicon to solar-grade silicon. The metallurgical route has the potential to become dominant in the production of solar-grade silicon. Polycrystalline solar-grade silicon sourced from the metallurgical route accounted for less than 8% of the total production in 2008 ²².

PRODUCTION OF CRYSTALLINE WAFERS

Once the high-purity silicon has been produced, the subsequent step involves converting it into thin sheets of good crystallographic quality, for use as solar cells. A thickness of about 100 microns is all that is needed to obtain the photovoltaic output from silicon¹⁸. Production of crystalline wafers can be achieved either by ribbon growth, or a two-step process starting with ingot casting or crystallisation followed by wafer manufacturing. Due to the overwhelming dominance of the latter process, and the minimal impact of the former process in industry, focus will be given to the two-step process, as detailed below.

Ingot casting (crystallisation)

The high-purity solar-grade silicon produced through refining undergoes a crystallisation step to minimise defects prior to the wafering process. Moreover, the dopant, *i.e.* phosphorus or boron, is added during ingot casting or crystallisation, for the important p-n junction needed for electricity generation. The product of this processing step is either a mono-crystalline silicon ingot or a multi-crystalline silicon ingot. Mono-crystalline silicon presents minimal defects and is of superior quality, which translates to higher solar-cell efficiencies in comparison to multi-crystalline silicon²³. Multi-crystalline silicon has a cost benefit over single crystalline silicon. The electronic industry only uses single crystalline silicon due to high quality requirements while both single crystalline and multi-crystalline silicon are used in the photovoltaic industry¹².

There exist several different techniques for ingot casting; the common crystallisation methods include the Czochralski process for single crystal ingots, and the Bridgman process for multi-crystalline silicon ingots²⁷. The Czochralski crystallisation process is used to convert polycrystalline materials into mono-crystalline materials. The Czochralski process is a batch process, where polysilicon is melted under vacuum to promote the evaporation of surface contaminants in a quartz crucible, which itself is located in a graphite crucible, and subsequently solidified on a mono-crystalline silicon seed crystal which is then slowly pulled out under rotation, producing a cylindrical mono-crystalline silicon ingot¹². It takes about two days to complete a production cycle of an ingot.

Most of the multi-crystalline silicon for the photovoltaic industry is produced by the crystallisation of liquid silicon in the form of a block; an example of such a process is the Bridgman process. The multi-crystalline ingot casting process entails melting solar-grade or polycrystalline silicon material in a crucible, and controlling the cooling rate. The crystal-liquid interface moves upwards from the bottom of the crucible. The temperature gradient and growth rate are controlled to favour the growth of a high-quality crystal structure, *i.e.* low thermal stresses. Generally, the goal is to obtain vertically aligned grains which indicate good directional growth. This unidirectional grain growth will avoid high thermal stress, and reduce the dislocation density in the multi-crystalline ingot. It will also ensure a consistent quality of the wafers, as the wafers are cut horizontally. Refining will also be achieved, as metal impurities will be pushed to the top of the ingot. The crucibles used are made of silica, and lined with a Si₃N₄ coating to prevent liquid silicon from sticking on the walls. Because of the multi-grained structure, the material is referred to as multi-crystalline, and the grains vary in size between several millimetres to centimetres.

Wafer manufacturing

Prior to wafer manufacturing, the ingots undergo sectioning where the peripheral sections are cut. The mono-crystalline cylindrical ingots undergo sectioning such that cubic ingots are produced, while multi-crystalline ingots are sectioned for the removal of highly contaminated peripheral regions. The

ingots are then cut to blocks with a cross-sectional area equal to the wafer size. About 25% and 15% of the material is lost from cutting of the mono-crystalline and multi-crystalline ingots respectively²⁴.

The silicon industry has been moving towards wafers of larger area. In the past, the standard size of silicon wafers was 10 x 10 cm², which was increased to 12.5 x 12.5 cm². At present, the majority of cells are 15.6 x 15.6 cm². The driving force for an increase in cell size is the decreasing cost per watt peak for increasing cell size.

Wafering of the blocks is carried out by multi-wire saw machines. In this cutting process, a single wire of stainless steel of typically 180 microns in diameter and several kilometres in length, is moved across the crystal in an abrasive slurry suspension, forming a wire web between two coils. Advantages of this method include high throughput and reduced wafer thickness. A wafer thickness below 200 microns is achievable in industry. Approximately 30% of the silicon is wasted as saw dust kerf loss²⁴. The plant layout for industrial production of crystalline silicon wafers at Monsanto Electronic Materials Company (MEMC) is shown in Figure 6, which details the main processing steps outlined above.

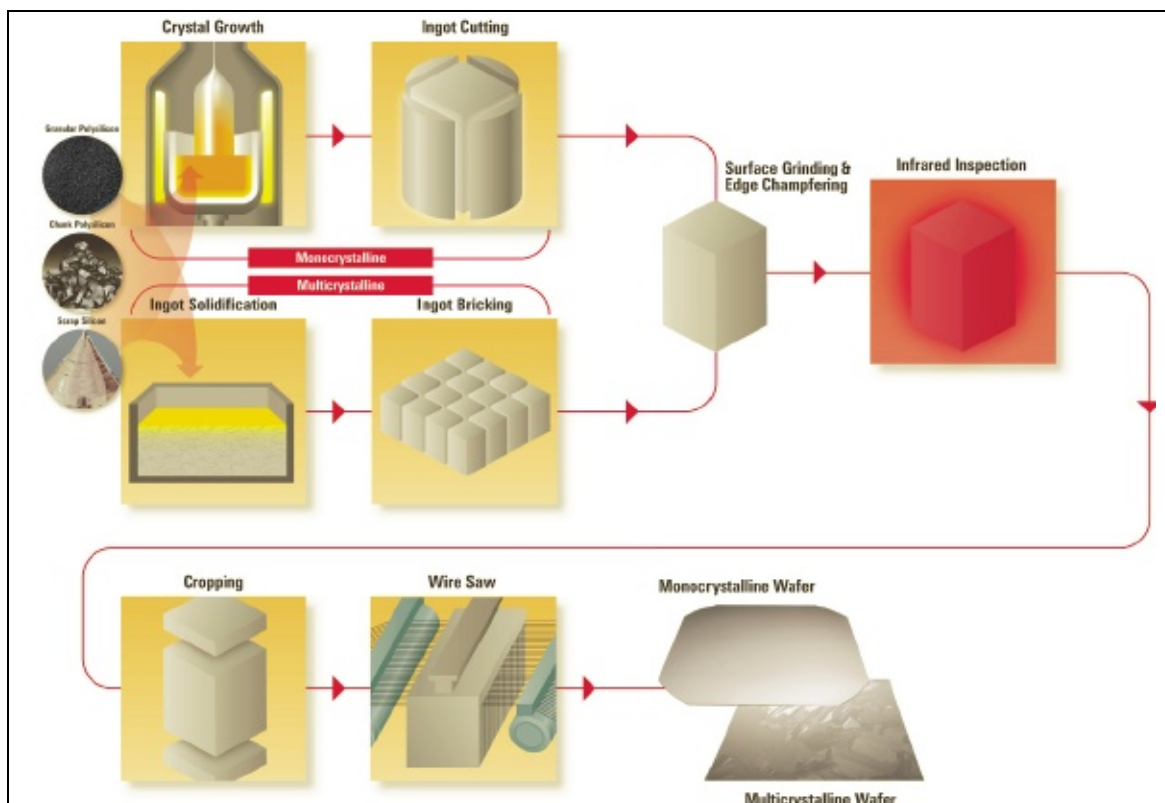


Figure 6: Typical plant layout: industrial production of crystalline silicon wafers²⁵

Wafer manufacturing makes up about 30% of the wafer cost²⁶. Moreover, the crystalline silicon wafer up to this stage of processing accounts for nearly half of

the final module costs²⁷. These costs show that there is potential to decrease the cost of producing crystalline silicon wafers.

SILICON SOLAR CELL MANUFACTURING

The silicon solar cell manufacturing step is important, both technically and economically, as endeavours can be undertaken during this step to minimize solar cell losses, *i.e.* maximize efficiency. Moreover, the silicon solar cell manufacturing costs account for approximately 25% of the final module cost. The production scheme for silicon solar cells is detailed below.

Saw-damaged layer removal

Silicon wafers usually contain a saw-damaged and contaminated surface layer, which has to be removed at the beginning of the solar cell manufacturing process. Typically, 10 to 20 microns is etched from both sides of wafers cut by a wire saw. Alkaline etches are commonly used, with subsequent rinsing in de-ionised water.

Texturing

Subsequent to etching, the silicon wafer surface is shiny and reflects more than 35% of incident light. The wafer surface therefore undergoes texturing in order to minimise reflectance. The reflection losses in commercial solar cells are reduced mainly by random chemical texturing. Mono-crystalline silicon wafers can be textured in a weak solution of sodium hydroxide and potassium hydroxide with additions of isopropanol at 80°C producing randomly distributed pyramids. Due to the nature of anisotropy in multi-crystalline silicon wafers, the random texturisation process is not effective on these silicon wafers. Mechanical texturing renders sound results for microcrystalline silicon wafer texturing. The optical reflection can be decreased to less than 10% in this processing step.

Emitter diffusion (junction formation)

Emitter diffusion is one of the critical steps in the manufacture of silicon solar cells. The starting silicon wafers are usually boron-doped, *i.e.* p-type. It follows that phosphorus, an n-type impurity, is introduced to form the p-n junction. The process is carried out in a furnace at a temperature of approximately 900°C for phosphorus diffusion. Typical processing time is limited to about 30 minutes, and a penetration depth of about 0.5 microns is achieved. A common dopant source is POCl₃. Other dopant deposition methods include screen printing, or chemical vapour deposition²⁷.

Edge isolation

During an n-type diffusion from the gas phase on p-type substrates, the emitter is usually formed on the entire surface of the wafer. Consequently, shunts are formed between the n-type and the p-type region of the silicon solar cell. Edge isolation techniques are applied to isolate the front and the rear side emitter. The techniques for edge isolation include mechanical, laser cutting, or plasma etching. Plasma etching is particularly synonymous with edge isolation of

screen-printed silicon solar cells. In plasma etching, the silicon wafers are stacked, and loaded into a vacuum chamber for etching in a fluoride or oxide plasma environment, and approximately 2 to 5 microns of silicon wafers are removed from the edges, thereby electrically isolating the front and the rear emitter²⁸. Careful handling of the silicon wafers is necessary to avoid damages.

Anti-reflection coating

The reduction in the front surface reflectance of a crystalline silicon solar cell presents a possibility for improved cell efficiency²⁹. An anti-reflection coating is applied to minimize surface reflectance. Several materials with refractive indices ranging between 1.4 and 2.7 can be used as anti-reflective coating on silicon solar cells³⁰. Titanium dioxide was the industrial choice for anti-reflection coatings. Currently, silicon nitride deposited by plasma-enhanced chemical vapour deposition is the dominant anti-reflection coating for silicon solar cells, due to its optimal refractive index and an additional benefit of bulk passivation properties.

Metal contact formation (metallisation)

The process of contact formation is a vital solar cell processing step because it strongly affects various properties of the silicon solar cell, such as short circuit current, open circuit voltage, series resistance, shunt resistance, and the fill factor³¹. The front side metallisation technique employed determines the shadowing and series resistance losses; the emitter diffusion profile and surface of doping concentration; as well as the choice of certain passivation techniques. For high-efficiency solar cells it is desired that front electrodes have low series resistance and low area coverage. The most widely used metal contacting technique for silicon solar cells is screen-printing³². This technology is simple, time saving, cost effective, and it reduces chemical wastes with little or no environmental impact. Moreover, this is a well-established technology that has been in practice since the beginning of the 1970s. The front side contacting is achieved by a screen-printed silver paste, while the rear side electrode formation and surface passivation are achieved by alloying a screen-printed aluminium paste with silicon. The pastes are subsequently dried in an oven at a temperature of approximately 300°C.

Contact firing

The screen-printed contacts initially lie on top of the insulating anti-reflection coating. The silicon solar cells undergo a short heat treatment at temperatures up to 900°C, using a belt-driven furnace. During the firing process, the anti-reflection coating layer experiences selective dissolution such that the contacts penetrate through the anti-reflection coating onto the emitter while avoiding deep penetration into bulk silicon. Moreover, the back surface field formation with aluminium is achieved³¹.

The production of crystalline silicon solar cells is complete. The PV industry reached solar cell production figures of 1 GW and 10 GW in 2004 and 2009 respectively, with crystalline silicon solar cells accounting for at least 80% of the market share³³. Moreover, the entire cumulative photovoltaic capacity until the

end of 2010 was almost 40 GW³⁴. Silicon solar cells with energy conversion efficiencies as high as 22% have been reported in industry³⁵. Prices for silicon solar cells are approaching \$1/W_p, while the most cost-effective solar modules have costs below \$1/W_p, and are made from CdTe thin films³⁶.

A crystalline silicon solar cell produces a voltage of about 0.5 volts. Therefore, individual cells are usually interconnected to produce a voltage useful for practical application. Moreover, the interconnected solar cells are encapsulated for protection, and in this way a solar module (panel) is produced. Such a solar module can be used directly for electricity generation or incorporated into a photovoltaic system. Energy payback time is about 1 to 2 years, while the module lifetime is about 25 to 30 years³⁴. The lowest cost for a crystalline silicon module is at about \$2/W_p³⁷.

CONCLUSIONS

The value chain for the processing of the most important material in photovoltaics, silicon, has been appraised. Silicon dominates the photovoltaic industry, particularly in its crystalline form. From a resource point of view, silicon is well placed as there are abundant reserves of silica in the earth's crust, and the production of metallurgical-grade silicon far exceeds the demand from the photovoltaic industry. Moreover, silicon is non-hazardous to both humans and the environment.

The overall message from the appraisal is that crystalline silicon has a high potential for cost reduction, and, to a lesser extent, higher conversion efficiency. This could be the winning formula for crystalline silicon, as feats with regard to cost reduction and higher energy-conversion efficiency will warrant sustainability and significance for crystalline silicon in the photovoltaic industry for years to come.

It was established that silicon is not necessarily the best material for solar energy conversion; therefore the future could see materials of high energy-conversion efficiency and low production costs. It would be desired that such materials are in abundance, environmentally friendly, and show long-term stability. The prospects of a sizeable 'green' contribution to electricity production from photovoltaics are good.

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REFERENCES

1. A.F.B. Braga, S.P. Moreira, P.R. Zamperi, J.M.G. Bacchin, P.R. Mei, New processes for the production of solar-grade polycrystalline silicon: A review, *Solar energy materials and solar cells*, volume 92, issue 4, 2008, pp.418-424.
2. M.A. Green, Crystalline and thin-film silicon solar cells: state of the art and future potential, *Solar energy*, vol.74, 2003, pp.181-192.
3. W. Hoffmann, PV solar electricity industry: market growth and perspective, *Solar energy materials and solar cells*, Vol.90, Issue 18-19, 2006, pp.3285-3311.
4. Global market outlook for photovoltaics until 2014, EPIA, January 2011.
http://www.epia.org/fileadmin/EPIA_docs/public/Global_Market_Outlook_for_Photovoltaics_until_2014.pdf
5. L. Zhang and A. Ciftja, Recycling of solar cell silicon scrap through filtration, Part 1: experimental investigation, *Solar energy materials and solar cells*, Vol.92, 2008, pp.1450-1461.
6. M. Di Sabatino, S. Binetti, J. Libal, M. Acciarri, H. Nordmark, and E.J. Øvrelid, Oxygen distribution on a multicrystalline silicon ingot grown from upgraded metallurgical silicon, *Solar energy materials and solar cells*, Vol.95, 2011, pp.529-533.
7. D. Sarti and R. Einhaus, Silicon feedstock for the multi-crystalline photovoltaic industry, *Solar energy materials and solar cells*, Vol.72, 2002, pp.27-40.
8. A. Goetzberger, C. Hebling, and H.W. Schock, Photovoltaic materials, history, status and outlook, *Materials science and engineering*, R.40, 2003, pp.1-46.
9. J.P. Murray, G. Flamant, and C.J. Roos, Silicon and solar grade silicon production by solar dissolution of Si_3N_4 , *Solar energy*, 80, 2006, pp.1349-1354.
10. J. Nelson, *Physics of solar cells*, Imperial college press, London, 2003.
11. J.J. Loferski, The first forty years: a brief history of the modern photovoltaic age, *Progress in photovoltaics: research and applications*, Vol.1, 1993, pp.67-78.
12. A. Goetzberger, C. Hebling, Photovoltaic materials, past, present and future, *Solar energy material and solar cells*, Vol.62, 2000, pp.1-19.
13. P. Woditsch and W. Koch, Solar grade silicon feedstock supply for PV industry, *Solar energy materials and solar cells*, Vol.72, 2002, pp.11-26.
14. S. Pizzini, Towards solar grade silicon: Challenges and benefits for low cost photovoltaics, *Solar energy materials and solar cells*, Vol.94, 2010, pp.1528-1533.
15. A. Schei, J. Tuset, and H. Tveit, Production of high silicon alloys, Tapir Forlag, Trondheim, 1998.
16. Globe specialty metals products – silicon, January 2011.
<http://www.glbsm.com/silicon-metal.aspx>
17. H.J. Möller, C. Funke, A. Lawrenz, S. Riedel, and M. Werner, Oxygen and lattice distortions in multicrystalline silicon, *Solar energy materials and solar cells*, Vol.72, 2002, pp.403-416.
18. M.A. Green, Solar cells: Operating principles, technology and system applications, Englewood cliffs, NJ, Prentice-Hall, Vol.94, 1982, pp.122-123.
19. D.C. Lynch and M.A. Lynch, The search for a low cost solar-grade silicon, *Silicon for the chemical industry VII*, Norway, 2004, pp.21-24.
20. REC group technology, January 2011.
<http://www.recgroup.com/en/tech/FBR/>
21. J.E. Bartlett, R.M. Margolis, and C.E. Jennings, The effects of the financial crisis on photovoltaics: an analysis of changes in market forecast from 2008 to 2009, *National renewable energy laboratory*, NREL Report no. TP-6A2-46713, 2009.
22. S. Price, R. Margolis, and J.E. Bartlett, 2008 solar technologies market report, Energy efficiency and renewable energy, U.S. Department of energy, 2010.
23. M. Komperød and B. Lie, Empirical modelling of heating element power for the Czochralski crystallization process, *Modeling, identification and control*, Vol.31, 2010, pp.19-34.
24. T. Markvart, Solar electricity, John Wiley & Sons, West Sussex, 2000.
25. MEMC, January 2011.
<http://www.memc.com/index.php?view=Solar-Manufacturing>
26. Ø. Mjøs, Directional solidification of silicon for solar cells, *Doctoral thesis: NTNU*, 109, 2006, pp.25-26.

27. T. Markvart and L. Castner, Practical handbook of photovoltaics: fundamentals and applications, *Elsevier*, 2003.
28. J. Arumughan, T. Pernau, A. Hauser, and I. Melnyk, Simplified edge isolation of buried contact solar cells, *Solar energy materials and solar cells*, Vol.87, 2005, pp.705-714.
29. L. Remache, E. Fourmond, A. Mahdjoub, J.Dupuis, and M. Lemiti, Design of porous silicon/PECVD SiO_x antireflection coatings for silicon solar cells, *Materials science and engineering*, Vol.176, 2011, pp.45-48.
30. R. Kishore, S.N. Singh, and B.K. Das, Screen printed titanium oxide and PECVD silicon nitride as antireflection coating on silicon solar cells, *Renewable energy*, Vol.12, 1997, pp.131-135.
31. T. Kwon, S. Kim, D. Kyung, W. Jung, S. Kim, Y. Lee, Y. Kim, K. Jang, S. Jung, M. Shin, and J. Yi, The effect of firing temperature profiles for the high efficiency of crystalline silicon solar cells, *Solar energy materials and solar cells*, Vol.94, 2010, pp.823-829.
32. D. Erath, A. Filipovic, M. Retzlaff, A.K. Goetz, F. Clement, D. Biro, and R. Preu, Advanced screen printing technique for high definition front side metallization of crystalline silicon solar cells, *Solar energy materials and solar cells*, Vol.94, 2010, pp.57-61.
33. Earth policy institute – solar power, January 2011.
<http://www.earth-policy.org/indicators/C47>
34. Solar Generation 6, Epia, February 2011.
<http://www.epia.org>
35. Sunpower – about us, February 2011.
<http://us.sunpowercorp.com/about/>
36. First solar – about us, January 2011.
<http://www.firstsolar.com/en/about.php>
37. Solar buzz – silicon, January 2011.
<http://www.solarbuzz.com/facts-and-figures/retail-price-environment/module-prices>



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