

Silicon processing: from quartz to crystalline silicon solar cells

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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 (eg, thin films) and third generation (eg, nanostructured solar cells).

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 century¹. Photovoltaic solar electricity presents an elegant means for electricity generation, as there are no moving parts, zero emissions, and no noise.

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 article.

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. Solar cells are assembled into solar modules for electricity generation.

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-Edmond 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 solidstate 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?

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.

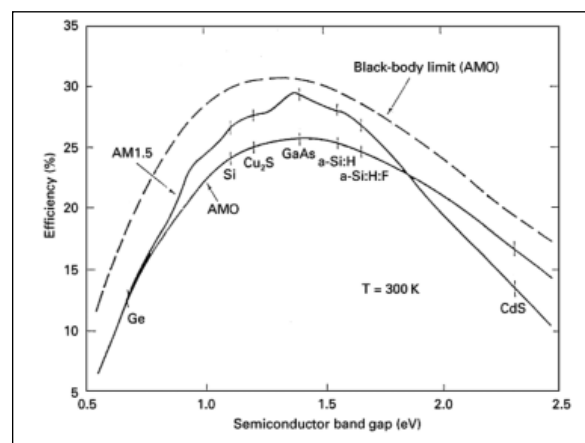


Figure 1: Solar cell energy conversion efficiency limits, as a function of the band gap of the semiconductor material, at different radiation¹²



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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 1).

The solar cell energy conversion efficiency limits shown in Figure 1 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.

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 2 shows a typical industrial silicon furnace.

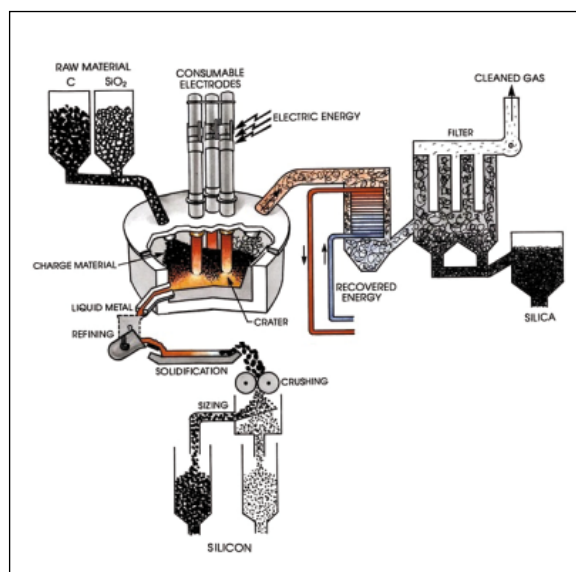


Figure 2: Typical plant layout: industrial production of silicon metal¹⁵

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 3.

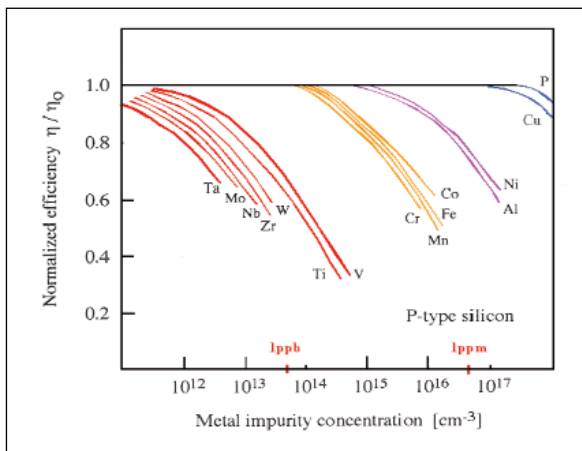


Figure 3: Silicon solar cell performance as a function of secondary impurities in p-type silicon¹⁸

The metal impurity concentration given in Figure 3 is expressed as the number of atoms of impurity per cm³. 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 3. 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 1: 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	1 500 - 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	3 000	<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.

Chemical route

The traditional Siemens process is the baseline process for the production of polysilicon. The production scheme is as follows: gasification of metallurgical-grade silicon, distillation, and deposition of ultrapure 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 ($T > 1\,100\text{ }^\circ\text{C}$) 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}.

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 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 acid⁴.

Metallurgical route

The metallurgical route entails obtaining solar-grade silicon directly from metallurgical-grade silicon via a series of metallurgical refining steps. 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 im-

purities 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, ie, purified quartz, carbon black, and high-purity electrodes; this renders low impurity levels in the upgraded metallurgical-grade silicon product.

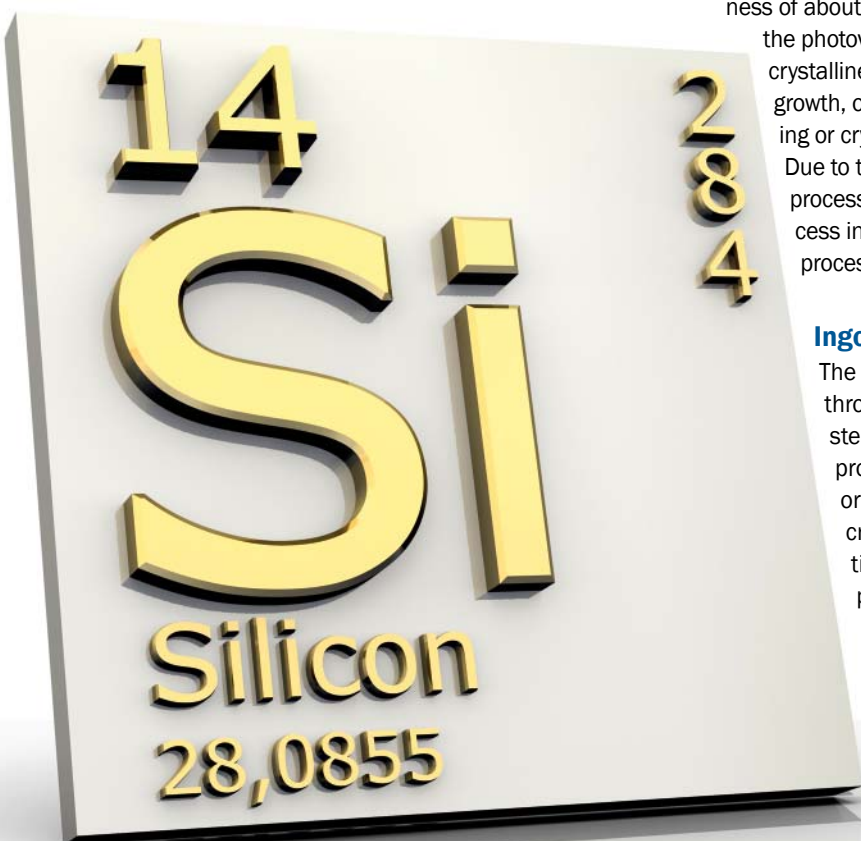
Since the refining techniques used in the metallurgical route tend to be effective in removing specific impurities, combinations of the refining steps are employed in industry for effective refining of metallurgical-grade silicon to solar-grade silicon. The metallurgical route has the potential to become 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 2008²².

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 crystallization 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 (crystallization)

The high-purity solar-grade silicon produced through refining undergoes a crystallization step to minimize defects prior to the wafering process. Moreover, the dopant, ie, phosphorus or boron, is added during ingot casting or crystallization, 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



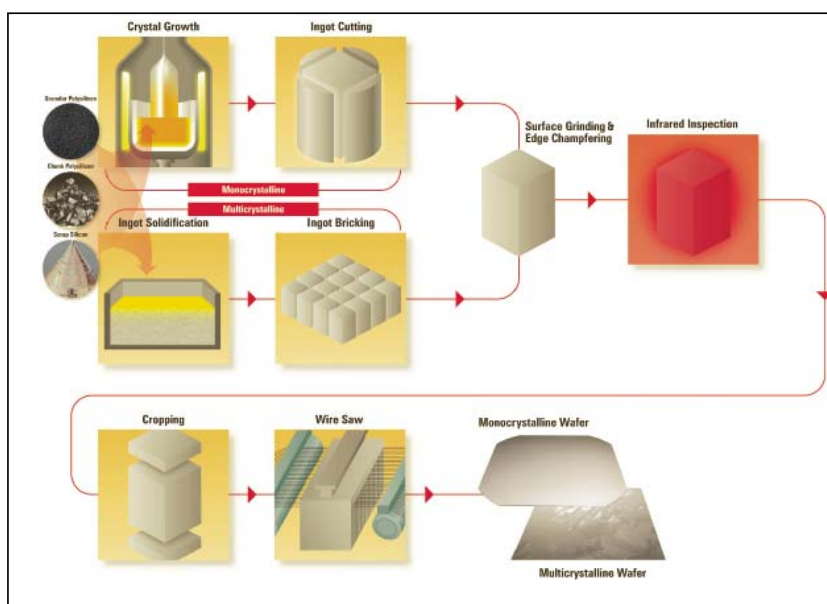


Figure 4: Typical plant layout: industrial production of crystalline silicon wafers²⁵

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 are several different techniques for ingot casting; the common crystallization methods include the Czochralski process for single crystal ingots, and the Bridgman process for multi-crystalline silicon ingots²⁷. The former process is used to convert polycrystalline materials into monocrystalline materials.

Most of the multi-crystalline silicon for the photovoltaic industry is produced by the crystallization 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.

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.

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, ie, 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 deionised 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 minimize 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.

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, ie, p-type. It follows that phosphorus, an n-type impurity, is introduced to form the p-n junction.

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.

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.

Metal contact formation (metallization)

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 metallization 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.

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 PV industry reached annual 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/Wp, while the most cost-effective solar modules have costs below \$1/Wp, 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/Wp³⁷.

Conclusions

The value chain for the processing of 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.

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.

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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