Overview of Manufacturing Processes For Solar-Grade Silicon

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May 6, 2011

Silicon, the second most abundant element in the earth's crust, is used in ~90% of worldwide PV installations where it represents approximately half of the cost of silicon solar cells. Advantages of using silicon for solar cells include: it's natural abundance, low-toxicity, a highly developed technology base owing to its widespread use in microelectronics, and a 25 + year projected operational life. This brief review describes how various grades of silicon are produced and a description of a new technology that holds promise of mass producing solar grade silicon with greater efficiency and at significantly lower prices than currently available.

Silicon does not naturally occur in its elemental form, but is usually combined with oxygen (as oxides) in the form of sand, rock, or quartz. To be useful in PV applications, these oxides must be converted to elemental silicon having very low levels of contaminants. Silicon is commonly classified according to its purity level. There are three grades of silicon: each reflecting a different level of contained impurities. The cost of silicon is inversely proportional to its impurity content. "Dirtier" or less pure silicon is quite inexpensive; highly pure silicon is the most expensive. These three grades of silicon are:

1. Metallurgical grade silicon (MG-Si)
   98% pure
   Used in alloying aluminum and steel and as raw materials in silicone industries
   Unsuitable for solar applications

2. Solar grade silicon (SG-Si)
   99.9999% pure (commonly called 6N or six nines pure)
   Used in PV applications

3. Electronic grade silicon (EG-Si)
   99.999999% (9N or nine nines pure)
   Used in making semiconductor wafers

To place these purity values in perspective, 99.99% "pure" gold is relatively impure and contains significantly more contaminants than either Solar Grade, SG, or Electronic

Grade, EG, silicon. For use in solar cells, however, even low impurity levels in silicon solar collectors can severely compromise mechanical and electrical properties as well as decrease solar cell conversion efficiencies. In these systems, impurities such as zirconium, titanium, and iron must be below 1 part per million by weight while levels of boron, phosphorus, and aluminum may not exceed 0.5 parts per million by weight. Therefore, MG-Si is not suitable for solar cells.

Unfortunately, higher purity 9N silicon, while slightly better in converting sunlight to electrical energy than lower quality 6N silicon, is quite costly. However, there is no primary source of lower cost 6N silicon for use in PV applications. The three silicon grades and their relative costs/availability are listed in Table 1.

TABLE 1

Cost/Purity for Various Types of Silicon

Silicon type	Metallurgical grade	solar grade	electronic grade
Designation	MG	SG	EG
Purity	98%	99.9999% 6 nines	99.999999% 9 nines
Performance In solar cells	inadequate	optimal	marginally better than solar grade
Approximate $/kg	$4	$15-50	$50
Availability	>1MM tons /yr	no dedicated producers	~150K tons /yr

Reducing silicon costs significantly improves solar cell economics via reduced costs of assembled solar modules. This could reduce solar electricity production costs potentially low enough to compete with conventional utility scale power generation in many regions. It is critical to develop an independent, dedicated, energy efficient silicon feedstock supply chain, to secure adequate supplies of low cost silicon to the PV industry. A secure supply of SG-Si at low cost is crucial for the PV industry. At present, the industry is dependent upon silicon prepared by the Siemens process (which will be described in detail below) which has been primarily used to make silicon for integrated circuits, power devices, and discrete semiconductor devices. This costly process keeps silicon prices high.

Alternatives to Using Silicon in Solar Cells

A number of solar collection technologies are not based on silicon. These technologies include: CIGS (copper indium gallium (de)selenide), CdTe (cadmium telluride), GaAs (gallium arsenide), printable organics, various electrolyte and organic dye solutions, iron sulfide, and nanoparticles. However, these proposed photovoltaic systems either suffer from limited supply of required raw materials needed to produce these systems, contain environmentally hazardous chemicals, have low solar collection efficiencies and unproven lifetimes, or have difficulty in being efficiently scaled to high production volumes at reasonable costs. These alternative technologies are not perceived by many solar industry specialists as a real challenge to replace silicon in solar collection systems.

How Silicon is Currently Manufactured

MG-Si is commercially produced (like many other metals) by removing oxygen from quartz in high temperature furnaces with the aid of suitable oxygen removing agents such as carbon. Generally in this carbothermic process, carbon and high temperatures (hence the name carbo+thermic) are used to remove oxygen and produce silicon according to the overall reaction:

Quartz + carbon (wood chips, coke) → silicon metal + carbon monoxide gas

In making MG-Si, approximately 12 kilowatt-hours of electrical energy are consumed per kilogram of silicon produced. This lowers silicon cost to a few dollars per kilogram. Currently, worldwide, approximately 700,000 tons of metallurgical grade silicon is produced yearly. Most of this output is used for producing aluminum and steel alloys and as components for the silicone industry. Because these starting materials (quartz, coke, wood) are not very pure, various contaminants remain in the silicon end product. However, for metallurgical applications these impurities are unimportant.

A. SIEMENS ™ Process to Produce Pure Silicon

The Siemens ™ process is the baseline process for the production of pure silicon. It accounts for essentially all SG-Si produced. This process begins by reacting powdered MG-Si with hydrogen chloride gas at around 800^{o}C under high pressure to form a mixture of gaseous chlorinated silicon compounds such as trichlorosilane. After a series of purification and fractional distillation steps, a high purity trichlorosilane is produced.

Mg-Si + hydrogen chloride → trichlorosilane + hydrogen
At high temperature (2000^{o}C)

This high purity trichlorosilane gas is subsequently decomposed to yield pure silicon and the hydrogen chloride is recovered. This process produces silicon of much higher purity than what is really necessary for solar panels. Energy consumption for the Siemens process is ~200 kilowatt hours/kilogram of silicon produced. Siemens type plants require large investments (~$170K /ton/yr) for relatively modest production capacities. This technology also involves production of toxic and corrosive compounds under high pressure and temperatures which require costly equipment made from heat-resistant and chemically inert materials.

B. SG-Si via Upgrading MG-Si

Since the 1970s a commonly proposed but as yet unsuccessful method to make SG-Si is to purify or upgrade inexpensive MG-Si. In this approach, various metallurgical purification and refining processes are used. These methods, which require less equipment and energy than the Siemens process include: bubbling selected gases through molten silicon, vacuum degassing to remove volatile impurities, or adding special collecting agents to extract and separate impurities from molten silicon. To date all UMG silicon does not have the required low level of impurities necessary for unblended use in the solar industry. Further the actual cost improvement per net unit yielded over the Siemens method has not been demonstrated. It currently represents a trivial fraction of silicon use in the industry.

C. SG-Si by Electrolysis

Electrolysis has been used for over 100 years to produce aluminum. Silicon can also be produced by electrolysis. Here, impure quartz is dissolved in a fluoride-containing melt at 1000°C, where it is decomposed into silicon and oxygen. Silicon precipitates at the electrode. The formed silicon is then crushed and cleaned with acid. In order to obtain a clean product, this silicon is melted and thereafter crystallized into ingots for subsequent sawing into wafers. The slag that comes with the silicon from the electrolyte has a high solubility for impurities and can be separated from silicon. This technique, however, has not been scaled to be capable of making multi-ton quantities of silicon with high efficiency. The fact that the silicon is not molten (as is the case of aluminum) increases the difficulty of scaling this process.

D. A New Technology Produces SG-Si via Purifying Water-Based Silicon Compounds

This is a new technology invented by the author of this article. The process was recently awarded a patent in the US and other countries, and is being commercialized by RSI Silicon which has produced solar grade samples. The company is starting commercial scale production this summer.

There is a bottleneck issue facing all producers of SG-Si based on carbothermic reaction of quartz and carbon - how are impurities removed from the formed silicon product? These impurities are introduced from the impure raw materials. Based on the extreme difficulties encountered in attempting to purify by UMG it would appear to be easier/cheaper to remove impurities from starting feed materials rather than trying to remove impurities once they are trapped in formed silicon. By utilizing the same proven high temperature furnace route used to manufacture inexpensive MG-Si, but starting with high purity feedstock, it is possible to directly produce high purity SG-Si at considerably lower cost. The basic chemical reaction would be identical to that which takes place when making inexpensive MG-Si except that now highly pure quartz together with highly pure carbon react in a clean environment to yield highly pure silicon. This approach has successfully produced SG-Si of sufficient purity at significantly lower cost than other methods.

The key to purifying starting raw materials lies in using water-based solutions of silicon and water-based carbon solutions and purifying them by utilizing similar proven technology used worldwide in large-scale water processing to selectively remove various metal and nonmetal species from water solutions. Purifying water solutions by passing it through ion exchange columns to remove impurities is widely used for water treatment at large scale. Various commercially available resins used in these ion exchange columns have high selectivity for selected impurity species and may be regenerated and reused many times. Because impurities removed from the silicon and carbon solutions are all at the part-per-million levels, these columns can process large volumes of liquids before needing to be regenerated.

An easily purified inexpensive silicon source is sodium meta-silicate dissolved in water. This commercially available solution, commonly called water glass, is produced by a number of companies worldwide via fusing silica sand with soda ash. This solution is widely used as a raw material in detergent industries and as cements for glass pottery and stoneware. This solution may be readily purified using ion-exchange resin technology to remove a host of metal impurities such as boron, phosphorus, aluminum, and iron (as well as other impurities that exist as water soluble salts) to well below the part-per-million levels. Once purified, this solution is dried and converted to highly purified, quartz-like material that is then used as a high purity feedstock in a furnace (similar to that used in making low cost MG-Si) thus replacing relatively impure quartz or sand.

High purity carbon, the other furnace feedstock, has also been successfully produced from abundant, cane/beet sugar. Sugar, currently at ~ $0.50/kg, is not only commercially available in very large quantities with very high purity, but since sugar is highly water soluble, it may be further purified by passing through ion exchange columns to obtain an extremely pure material. This highly pure sugar solution, when dried and carbonized, yields a pure carbon source which can replace impure coal or wood.

By combining this highly purified quartz with highly purified carbon in a specially designed clean furnace (to minimize introduction of impurities), SG-Si may be produced with the high efficiencies, low cost, and simplified furnace design associated with making MG-Si. Combining the well known inexpensive processes for making MG-Si with ion exchange technologies to create high purity starting materials has been successfully demonstrated. In this new process, raw materials are abundant and easily purified, the process is scalable with lower production and entry costs than current methodologies, it does not involve hazardous or flammable materials, and it produces high purity silicon with less than 1 part per million of undesirable metal contaminants. In addition, the process can utilize renewable feedstock and is near carbon neutral.

Conclusions

There are a number of processes presently proposed for making solar grade silicon for the PV industry. Future prospects for the PV industry are very promising provided low cost, high purity silicon supplies remain adequate. The phenomenal growth in the industry will provide great opportunities for a new silicon process that could achieve the aforementioned goals of low cost, low energy use, renewable, carbon neutral and with a low capital investment.

About the author

Steven Amendola is the founder and President of RSI Silicon LLC, a silicon producing startup located in Easton, PA. He has over 30 years of experience in materials science, metallurgy, catalysis, alternative energy and electrochemical systems. Steve has received more than 25 US patents and published numerous technical papers in scientific journals. He holds a B.A. in Chemistry (1978) from The King's College and a graduate degree in Chemistry (PhD-ABD) from Ohio State University. He may be reached at amendol1@verizon.net.

Acknowledgement

The author thanks David Gelbaum of the Quercus Trust, the Mandor family, Michael Oster and Lyle Rawlings for their unwavering belief and financial support in RSI's paradigm shifting silicon technology to advance the solar industry.