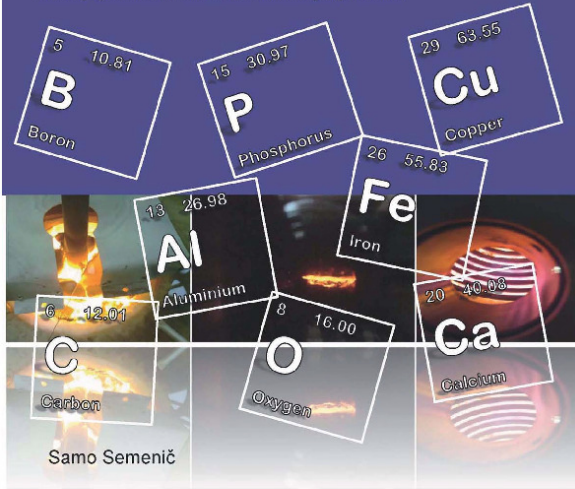




Samo Semenic (Autor)
Upgraded metallurgical silicon for application in the photovoltaic industry

Schriftenreihe des Lehrstuhls für Kontinuumsmechanik und Materialtheorie
der Technischen Universität Berlin

Herausgegeben von Prof. Dr. rer. nat. Wolfgang H. Müller



**UPGRADED METALLURGICAL SILICON FOR
APPLICATION IN THE PHOTOVOLTAIC INDUSTRY**



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1 Introduction

Silicon is found in nature in the form of oxides and represents 1/3 of the crust of the Earth. It has the same crystallographic structure as diamond. It is chemically bound in weathered and no-weathered rocks (granite, gneiss, porphyry, and kaolinite) in the form of oxides and silicates.

Quartz is one type of silicon oxide and a component of various rocks, but it is also an important source for the manufacture of silicon and its compounds. Table 1.1 shows some general, physical and chemical structural properties of silicon.

Table 1.1: General properties of silicon.

Symbol	Si
Atomic number	14
Atomic weight	28.086 g/mol
Physical state	solid
Description of appearance	gray, slightly shiny metal hard, brittle crystals



Figure 1.1: Silicon metal [1].

1.1 History

Antoine-Laurent de Lavoisier discovered silicon in 1787. First impure silicon has probably been prepared through the heating of potassium (K) with silicon tetrafluoride (SiF_4). In 1824 Jöns Jacob Berzelius has generally been given credit for discovering the element silicon. He has used the same method which was used by Joseph Louis Gay-Lussac and Louis Jacques Thénard when they got amorphous silicon. By repeatedly washing he got very pure silicon.

In 1854 the first crystalline silicon was made, accidentally, by Sainte-Claire Deville. The first preparation of silicon/silicon rich alloys in an electric arc furnace was performed by Moisan in 1895. Independently, Bozel, and Rathenau prepared silicon for industrial production in the period 1897 to 1898.

Silicon alloys, particularly ferroalloys – FeSi with Si in range 15 % till 90 % Si played an important role in the production of steel at the end of the nineteenth century.

Silicon carbide (SiC) had also found a range of applications taking advantage of its hardness and chemically noble character. More recently SiC has found applications in electronics because of its excellent semiconductor properties. It tends to become a strategic material for cutting silicon into thin wafers.

1.2 Applications

Silicon is stable and has a strong affinity for oxygen, forming stable oxides and silicates, the only natural occurrences known for silicon. Elemental silicon immediately oxidizes, forming a thin protective film of silicon dioxide of less than 100 Å. A thin film of oxide prevents further oxidation.

Silicon and carbon form a strong Si–C bond and stable products. Silicon carbide is artificially synthesized in several allomorphic structures, finding various applications in photovoltaic and electronics. Primary use is made of the abrasive properties of SiC for wafering silicon crystals and the emerging applications of SiC semiconductors.

1.2.1 Applications in the aluminum industry

In the aluminum industry silicon is added to molten aluminum in which it is dissolved. A simple eutectic composition occurs at 12.6 % silicon in aluminum. Silicon is used to improve the viscosity, the fluidity of liquid aluminum and the mechanical properties of commercial alloys. The iron, calcium and phosphorus content in silicon are particularly critical for such applications.

1.2.2 Applications in chemistry

1.2.2.1 Silicones

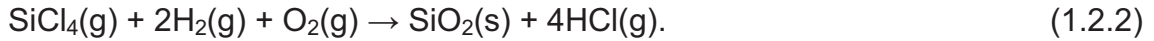
Since the discovery of direct synthesis of dimethyldichlorosilane the silicones industry has developed to a strong and growing chemical business:



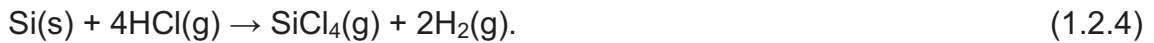
The direct synthesis of dimethyldichlorosilane is industrially performed in a fluidized bed reactor requiring small particles or powder of silicon (20–300 µm). The reaction is exothermic and needs to be activated with copper catalysts as well as promoters such as Zn, Sn, P and others. Whereas Fe does not seem to play an important role, Ca and Al have shown to take an active part in the overall reaction.

1.2.2.2 Synthetic silica

Varieties of synthetic silicon oxide (silica), such as pyrogenic silica (also called fumed silica) or silica ingots as feedstock to optical fibers are industrially prepared by burning silicon tetrachloride:



Silicon tetrachloride may be prepared by chlorination of natural silica. However, industrially, silicon tetrachloride is produced by reacting chlorine with metallurgical grade silicon in a direct synthesis performed either in a fluidized bed or in a fixed bed reactor:



The main market for fumed silica as additives in silicone rubbers is used to increase the mechanical strength and the elasticity of these elastomers.

1.2.2.3 Functional silane

This generic term covers a broad range of products built on silane molecules, in which an atom of hydrogen or of chlorine is substituted with an organic radical bearing a functional group, for example, amine, acid, ester, alcohol, and so on.

In one of the most important applications it is used as a coupling agent between inorganic and organic compounds, for example, inorganic fillers (glass, silica, clays, *etc.*) in organic matrices (epoxy, polyester, *etc.*)

1.2.3 Semiconductor silicon

Commercially available metallurgical grade silicon (M-Si) typically contains 10,000 ppmw impurities, whereas high purity silicon (HP-Si) is of very high purity (low ppb impurities). Solar grade silicon (SoG-Si) should be roughly in the range of 1 ppmw total impurities, which is hundreds to a thousand times less pure than high purity silicon, but approximately 10,000 times more pure than metallurgical grade silicon. Metallurgical grade silicon, produced by carbothermic reduction of silica in a submerged electrode arc furnace, is abundantly available at low cost (~ \$1.50/kg), but is unsuitable for photovoltaic applications. High purity silicon is produced specifically for the semiconductor industry using multiple distillations of silane. This material is expensive (> \$60/kg stable price), and at the same time it is of a higher purity than it is required for photovoltaic industry. However, the current process for producing high purity silicon produces unnecessarily pure material for photovoltaic purposes. What is needed is a technique that can produce silicon in the range of 1 ppmw total impurities. The specifications for abundantly available metallurgical grade silicon, high purity silicon, and solar grade silicon are shown in Table 1.2.

Table 1.2: Impurity concentration in different silicon grades [2].

Impurity concentrations (ppma)			
Impurity	M-Si	SoG-Si	HP-Si
B	37-45	0.5	0.0002
Al	1,200-4,000	<0.1	<0.0008
P	27-30	0.05	0.0008
Ca	590	0.05	<0.003
Ti	150-200	<0.1	<0.003
V	100-200	<0.1	<0.003
Cr	50-140	<0.1	<0.003
Mn	70-80	<0.1	<0.003
Fe	1,600-3,000	<0.1	<0.010
Ni	40-80	<0.1	<0.010
Cu	24-90	<0.1	<0.003
Zr	30	<0.1	<0.010
Mo	<10	<0.1	<0.003

Since the emergence of solid-state electronics, in the late fifties and early sixties, silicon is by far the most important and popular semiconductor material. Ultra-pure silicon with the adequate semiconductor properties is industrially prepared through distillation and thermal decomposition of volatile silicon compounds, for example, trichlorosilane, SiHCl_3 , and monosilane, SiH_4 . These operations are performed in large chemical plants which for synergy reasons are sometimes incorporated in plants producing other silicon-based compounds as those described above. Although the ultimate application in the case of polysilicon is in the semiconductor industry, this particular process is, from a silicon raw material perspective, counted among the chemical applications of silicon.

1.2.3.1 Mono-crystalline silicon

Silicon solar cells were first made about sixty years ago from Czochralski (Cz)-pulled mono-crystals using a technology adapted from the microelectronics industry: Figure 1.2.

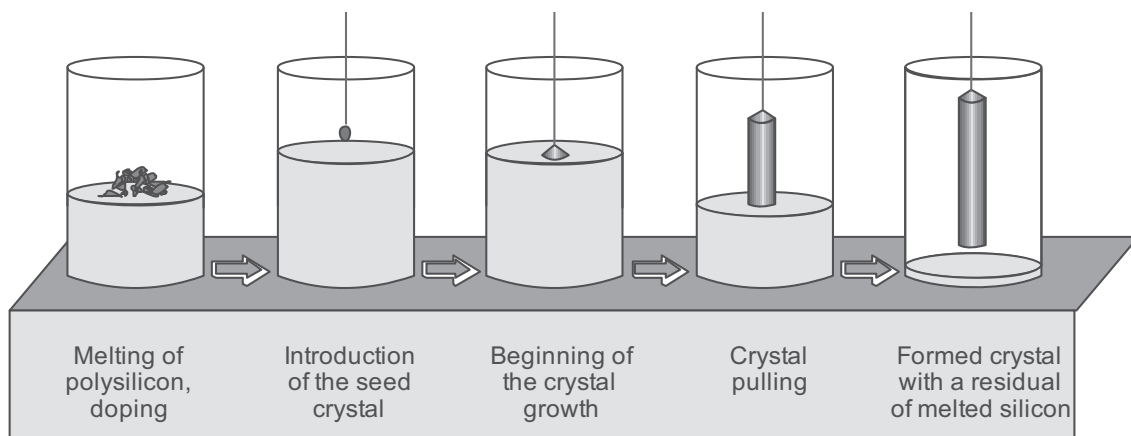


Figure 1.2: Czochralski ingot grows [3].

The dominant absorber material used today for the majority of commercially produced solar cells is Czochralski-grown crystalline silicon (c-Si) in mono-crystalline and block-cast material in multi-crystalline form (mc-Si). Up to now a lot of effort has been undertaken to increase the electrical efficiency of solar cells reproducibly toward and even above 20 %.

Efficiency improvements are often reached only with the help of cost-intensive process steps so that most steps cannot be directly implemented into industrial products but have to be reengineered for low-enough cost.

Subsequently, world-record cell efficiencies have been achieved at a very high cost on a laboratory scale with Float Zone (FZ) mono-crystalline: Figure 1.3.

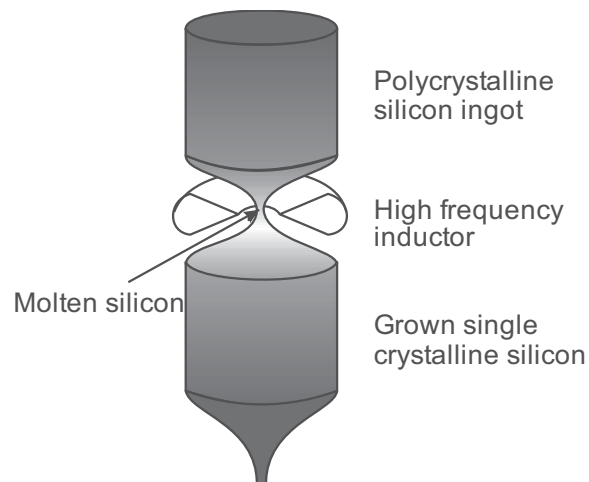


Figure 1.3: Float zone ingot grows [4].

Hence there still remains a significant efficiency gap between mono-crystalline laboratory cells with photovoltaic efficiencies up to 24 % and cost-effective, commercial Czochralski solar cells that are presently produced and sold in high volume at approximately 14 % to 17 % photovoltaic efficiency.

1.2.3.2 Multi-crystalline silicon

Multi-crystalline silicon besides mono-crystalline silicon represents the basis of today's photovoltaic technology. Multi-crystalline silicon offers advantages over mono-crystalline silicon with respect to manufacturing costs and feedstock tolerance at, however, slightly reduced photovoltaic efficiencies. The efficiencies of multi-crystalline silicon solar cells are affected by recombination-active impurity atoms and extended defects, such as grain boundaries and dislocations. A key issue in achieving high solar cell efficiencies is a perfect temperature profile of both ingot fabrication and solar cell processing in order to control the number and the electrical activity of extended defects. Moreover, the implementation of hydrogen-passivation steps in solar cell processing turned out to be of particular importance for multi-crystalline silicon. With the introduction of modern hydrogen-passivation steps by Si_3N_4 layer deposition, the efficiencies of industrial multi-crystalline silicon solar cells were boosted to the 14 % to 15 % efficiency range and consequently market shares

were continuously shifted towards multi-crystalline silicon as the standard material of photovoltaic.

Standard multi-crystalline silicon is a boron-doped p-type material with a specific electrical resistivity of about $1 \Omega\text{cm}$, which corresponds to a boron concentration of about $2 \times 10^{16}/\text{cm}^3$. The specific resistivity is adjusted in such a way that optimal solar cell performance is guaranteed. Naturally, the boron concentration can be varied according to the requirements of specific solar cell processes. Specific resistivity in a range of 0.1 to $5 \Omega\text{cm}$ has been used for solar cell fabrication so far: Figure 1.4.



Figure 1.4: Multi-crystalline ingot [5].

1.2.4 Thin film solar cell

This is a solar cell made by deposits of one or more thin layers of silicon on a substrate. The layer thickness range is wide and varies from nanometers up to a few tens of micrometers. For manufacturing Thin-Film Solar Cells (TFSCs), also called Thin-Film Photovoltaic Cells (TFPVs), many different photovoltaic materials deposited with various deposition methods on a variety of substrates can be used. The TFSC are categorized according to the photovoltaic material [6]:

- Amorphous silicon (a-Si) and other thin-film silicon (TF-Si),
- Cadmium Telluride (CdTe),
- Copper indium gallium selenide (CIS or CIGS),
- Dye-sensitized solar cell (DSC) and other organic solar cell.

Amorphous silicon (a-Si) cells are a thinner version of the traditional silicon-wafer cell. One of the biggest problems with a-Si solar cells is their photovoltaic efficiency. These cells are subject to significant degradation in power output when they are exposed to the sun. By reducing the thickness of the solar cells, these degradation issues can be overcome, however, thinner layers also absorb sunlight less efficiently. As a result a-Si photovoltaic cells are perfect for smaller-scale applications, such as calculators, but less than ideal for larger-scale applications, such as solar-powered buildings.

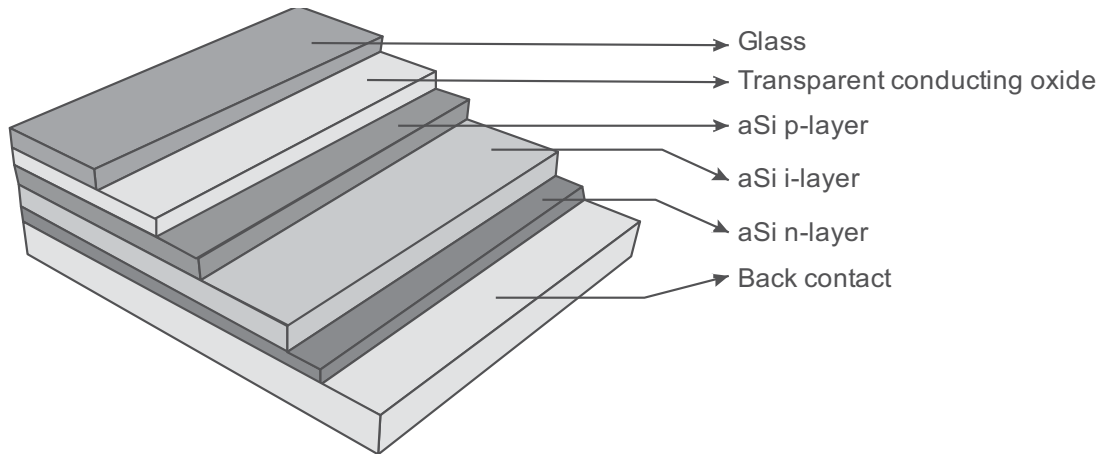


Figure 1.5: Amorphous silicon thin film photovoltaic cell [7].

Compared to Si photovoltaic cells (see Figure 1.5), Copper, Indium, Gallium, and Selenium (CIGS) thin film photovoltaic cells (see Figure 1.6) have been able to reach higher photovoltaic efficiencies. These cells operate similarly to conventional crystalline silicon solar cells. When light hits the cell it is absorbed in the CIGS and thus creates free electrons and holes. These electrons diffuse in the CIGS grains until they reach the electric field within the junction region. At this point they are driven into the cadmium sulfide / zinc oxide (ZnO), which leads to a buildup of voltage between the ZnO electrode and the molybdenum (Mo) base, Figure 1.6.

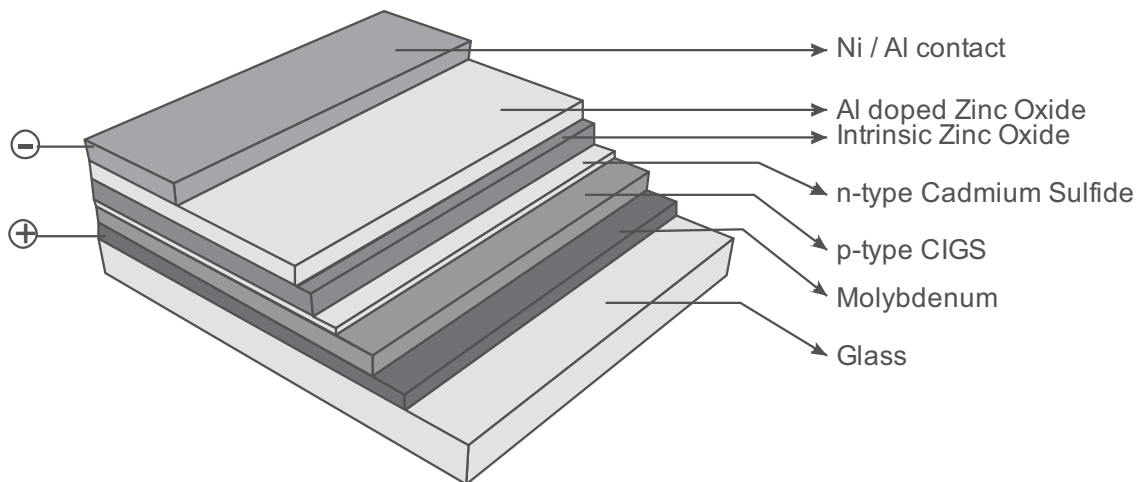


Figure 1.6: Copper, Indium, Gallium, and Selenium (CIGS) thin film photovoltaic cell [8].

1.3 Market

"The 20th century was about the globalization of energy with the world dependent on a few powerful oil producers. However, this century will witness the localization of the world's energy economy, as countries tap renewable energy resources -- wind, solar and geothermal power -- much closer to home." [9] (see also Figure 1.7).

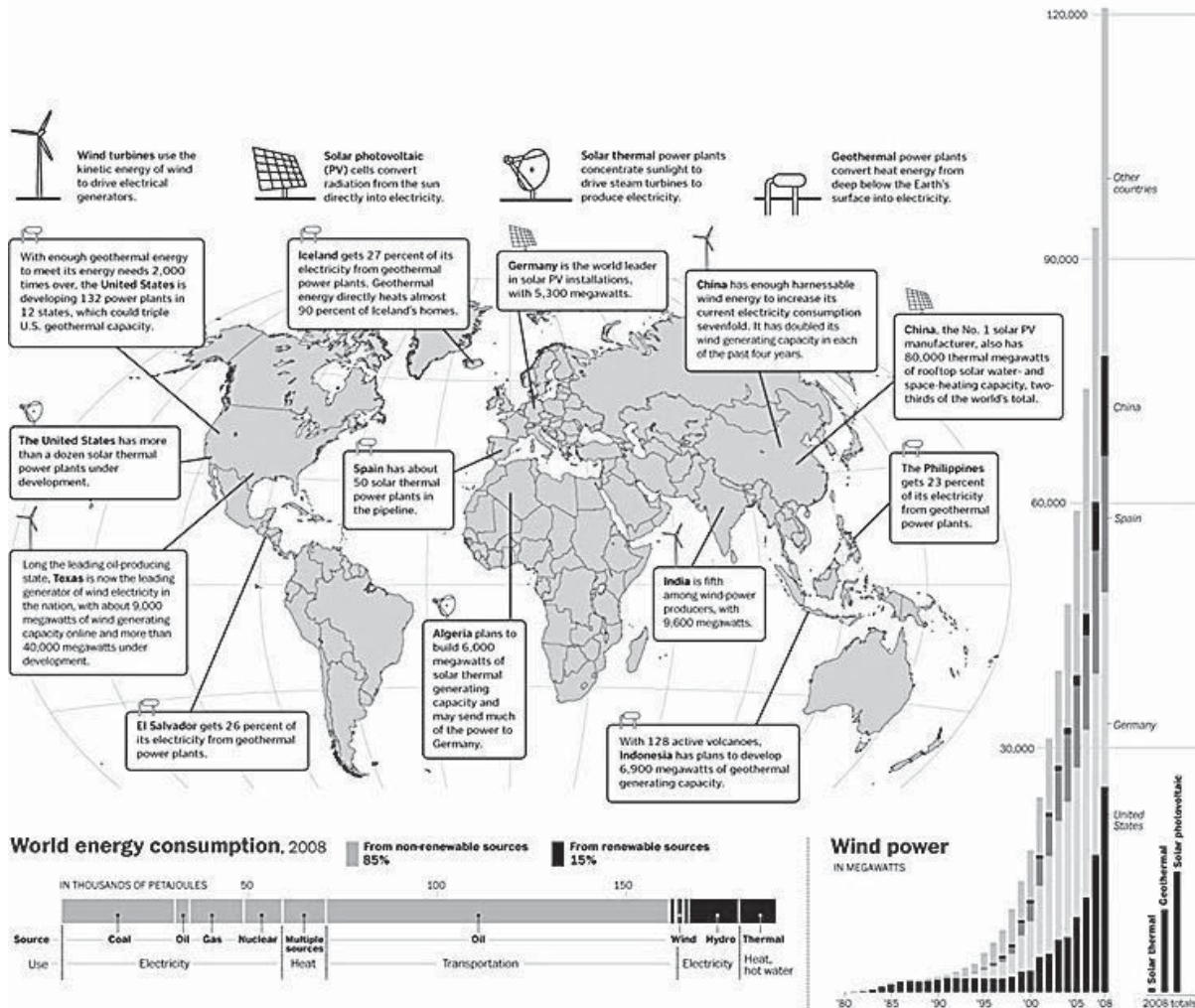


Figure 1.7: World energy consumption [10].

The present-day renewable-energy industry is an energy industry of new and appropriate technologies. Worldwide investors have paid much greater attention to this emerging renewable energy industry in recent years. In many cases this has translated into rapid commercialization and considerable industry expansion. The solar industry provides a good example of this.

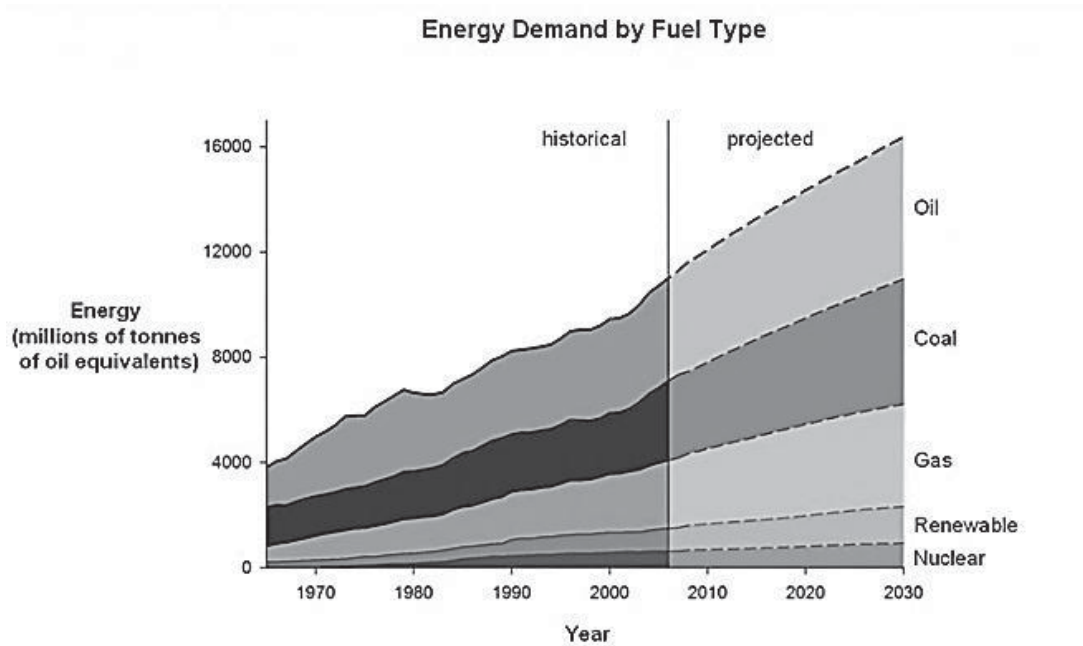


Figure 1.8: Energy demand by fuel type [11].

Energy consumption projection for the next period shows further growth of all kind of fuel: Figure 1.8.

The production starts with silicon metal which is the material used to gain high purity. High purity silicon is used for growing silicon ingots which will be sliced to wafers in a process called wafering. Compositionally pure mono or multi-crystalline silicon wafers are useful for photovoltaic purposes. Dislocation-free and extremely-flat mono-crystalline wafers are required for the manufacture of computer chips: Figure 1.9.

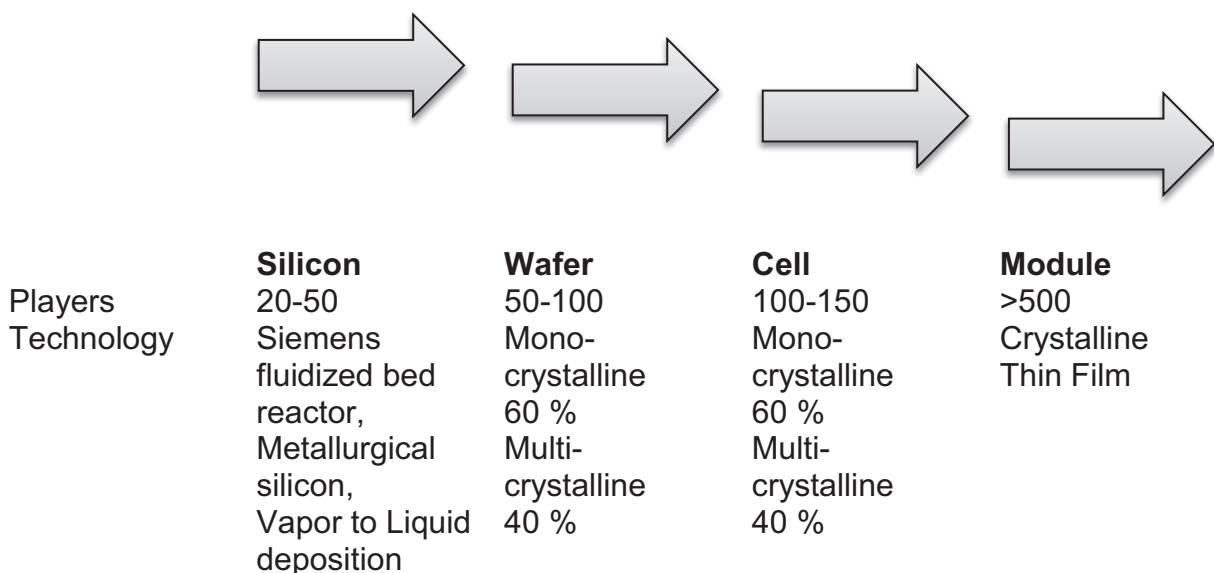


Figure 1.9: Production chain [12].

Many silicon producers use several different stages of production processes. Some of them are listed below [13]:

- Silicon metal producers
 - Elkem Solar
 - Globe speciality metals
 - Fesil
 - JFE steel
 - REC – Renewable Energy Corporation
 - Nitol Solar
 - UC Rusal
 - Ferroatlantica
- High purity Silicon
 - Hemlock Semiconductor Corporation
 - REC
 - Wacker Chemie AG
 - Origin of Chemical Innovation – OCI
 - GLC
 - Timminco
- Silicon wafer manufacturers
 - Siltronic AG
 - Sumco (Mitsubishi/Sumitomo Sumco Silicon)
 - MEMC Electronic Materials
 - LDK Solar
 - Zhejiang DC Chemical
 - REC
 - Renesola
 - Tokuyama
 - Topsil
 - Shin-Etsu Handotai Chemical Company

According to the annual market survey, done by the photovoltaic trade publication Photon International, the global production of photovoltaic cell in year 2009 was 12.3 GW. The top ten companies produce app. 45 % of the total production and are [14]:

- Photovoltaic manufacturers

○ First Solar	1,100.0 MW
○ Suntech	704.0 MW
○ Sharp	595.0 MW
○ Q-Cells	586.0 MW
○ Yingli	525.3 MW
○ JA Solar	520.0 MW
○ Kyocera	400.0 MW
○ Trina Solar	399.0 MW
○ Sun Power	397.0 MW
○ Gintech	368.0 MW

In total the global production of thin films represents 16.8 %. Some of thin-film manufactures are listed below with its capacity.

- Thin film manufacturers

○ First Solar	1100.0 MW
○ United Solar Ovonic	123.4 MW
○ Sharp	94.0 MW

○ Sunfilm	60.0 MW
○ Trony	50.0 MW
○ Solar Ffrontier	43.0 MW
○ Mitsubishi	42.0 MW
○ Kaneka	40.0 MW
○ Moser Baer	40.0 MW
○ Würth Solar	30.0 MW
○ Bosch	30.0 MW
○ EPV	30.0 MW
○ Solyndra	30.0 MW

1.4 Trends

1.4.1 Production increase

The demand for polysilicon from the solar industry has been growing and is expected to continue increasing. Solar demand polysilicon had a 38 % growth from 2002 to 2008 and is expected to have a 30 % growth from 2008 to 2015: Figure 1.10.

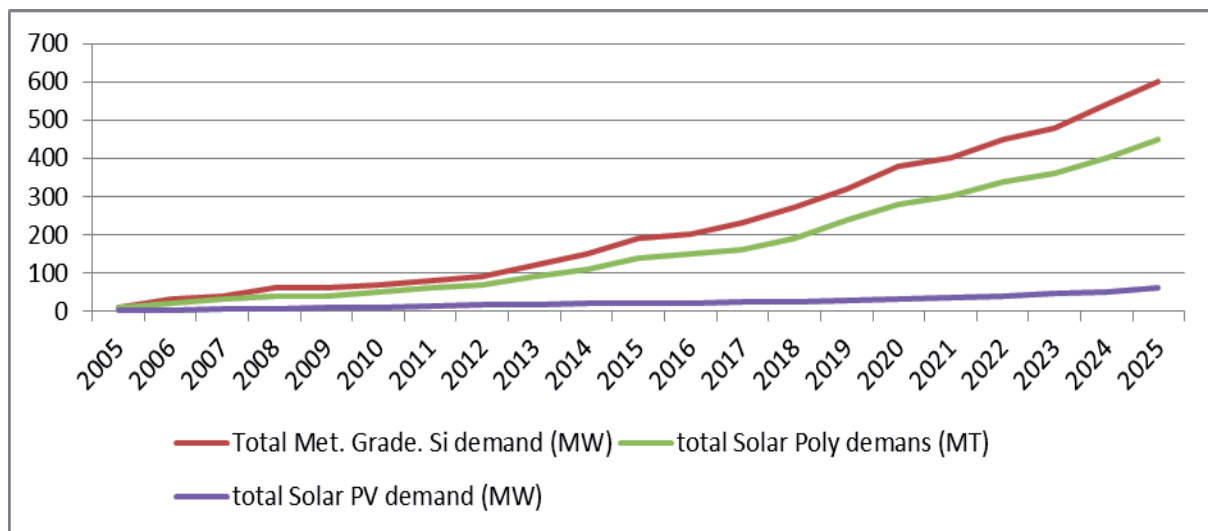


Figure 1.10: Silicon market demand [15].

1.4.2 Upgraded metallurgical silicon

Alternative methodologies of silicon processing include enriching purity levels sufficient for photovoltaic usage have gained increasing levels of attention in recent years. Metallurgical silicon (m-Si) is a commodity that is currently used in the traditional Siemens reactor silicon production process. In this process m-Si is gasified and used as part of trichlorosilane gas which is injected into the deposition furnaces. Under the process developed by Elkem, Timminco, and several others, raw m-Si is not gasified but purified directly into solar grade silicon. The benefit is the elimination of the gasification step, which could result in an end product whose production cost is 30–50 % cheaper than the silicon produced in the traditional Siemens-reactor process, and capacity could be brought online much faster than for a traditional Siemens process.

Historically, the upgraded metallurgical silicon process itself was too expensive and yielded cells with conversion efficiency and quality levels that were inadequate for photovoltaic usage. However, recent advances in the economics of the process, as well as learning curve experience working with upgraded metallurgical silicon wafers on pilot lines, have allowed certain manufacturers to begin selling photovoltaic cells made with upgraded metallurgical silicon, raising the question of whether or not tight silicon availability will remain a risk in future cycles going forward.

Cell manufacturers such as Q-Cells and Canadian Solar are reporting good progress using upgraded metallurgical silicon wafers from Elkem and Timminco to make cells with conversion efficiency levels as high as the mid-teens for 100 % upgraded metallurgical silicon. Yet we note that reported yield levels from upgraded metallurgical silicon factories have been very low compared to normal polysilicon, and that upgraded metallurgical silicon wafers cannot currently be used to manufacture higher range conversion efficiency cells. Since small changes in conversion efficiency can drive significant changes to gross margins, switching from normal polysilicon to upgraded metallurgical silicon would only make economic sense if the presumed loss in gross margin (due to a drop in conversion efficiency) for an installed photovoltaic system is more than offset by the cost reduction of upgraded metallurgical silicon versus polysilicon. Additionally, we are concerned that the low conversion efficiency and lower purity of upgraded metallurgical silicon could lead to higher conversion (transforming raw silicon to wafer to cell to module) costs. Lower efficiency modules will likely be sold at a discount to traditional, higher efficiency modules, and, in an environment characterized by spiraling polysilicon prices, the value proposition for upgraded metallurgical silicon as an attractive alternative to polysilicon may no longer hold true.

1.4.3 Pricing impact

Given the potential for additional silicon supplies to hit the market in the coming months/years and the current uncertainty around the growth in the size of the various incentive pools available for solar silicon, we project that photovoltaic system prices will need to fall faster than the build-in rate of digression in key markets, like Germany, to create sufficient demand to absorb the supply of modules coming on, given the lack of accurate aggregate data available for silicon production being sold to photovoltaic cell and module manufacturers.

1.4.4 Cost reduction opportunities

In most photovoltaic markets, incentives are expected to decline over time to “force-wean” the solar industry off subsidies that were meant to encourage scale economics. Thus in order to keep adoption rates high through attractive equity rates of return and pay-back periods, installed solar costs (not just modules) will need to drop at least sufficiently to offset the decline in incentives. In markets like Germany, where feed-in tariffs are structured on a declining scale, this allows strong visibility into the need to cut installed system prices. Yet, in practice, gyrations in demand resulting from the introduction of new incentives in other (competing) markets can create the opposite effect, with system prices rising as subsidies fall. Against a backdrop of declining system prices, photovoltaic manufacturers are targeting

aggressive cost reduction opportunities related to scale, silicon costs, conversion efficiency levels, and vertical integration. As the industry grows, the opportunity to source materials and equipment from multiple suppliers in larger volumes also grows, allowing for scale benefit opportunities. In Figure 1.11 below, a cost reduction request of at least 50 % by 2012 compared to 2006 is shown. We note the prominence of downstream savings in the overall mix which we believe may be among the most difficult to accomplish without more vertical integration and consolidation of market share in that segment.

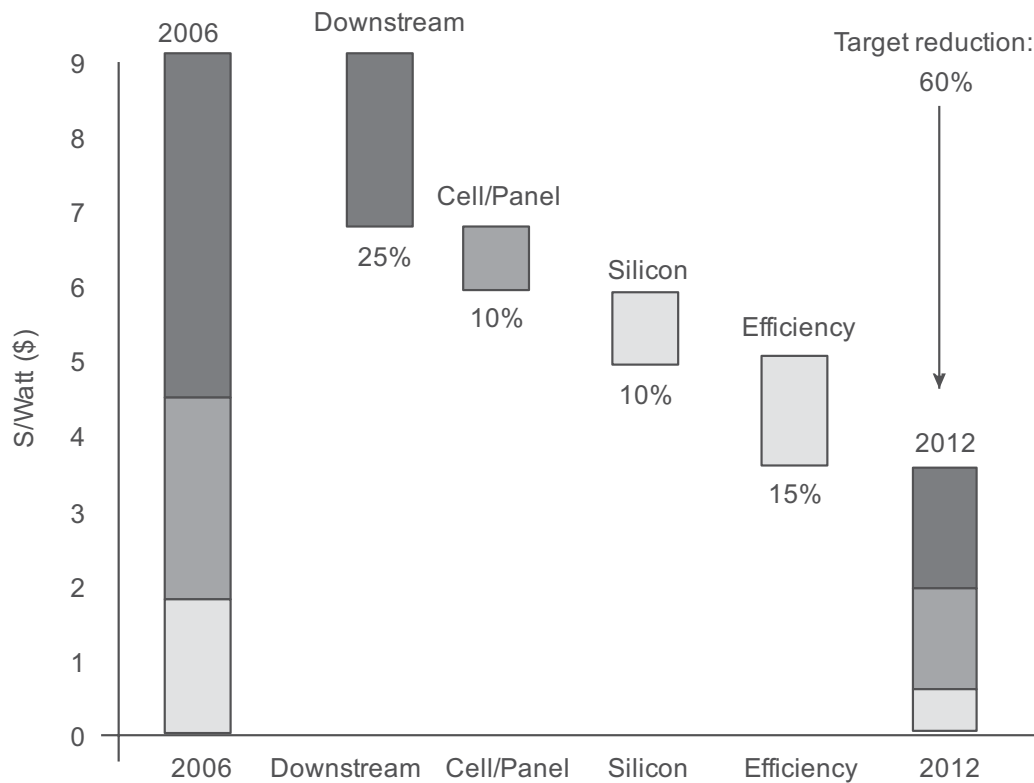


Figure 1.11: Sun power cost reduction targets.

1.4.5 Silicon photovoltaic efficiency

Crystalline silicon solar cells represent about 90 % of the total solar market and rely on silicon as the key feedstock. The surging demand for solar cells has led to a jump in silicon prices. As recently as 2005, solar companies could secure feedstock at \$30–\$50/kg, while current new silicon supply contracts are being priced at levels around \$60–70/kg and many have pricing mechanisms with links to moves in a basket of spot prices (although not priced at spot-type rates). On a spot basis, the price for polysilicon had exceeded \$500/kg (for high-quality silicon that is blended with lower-quality scrap) in early 2009 but has since fallen to \$50–\$70/kg.

In this context, cell and module producers look for ways to maximize their output by increasing conversion efficiency levels as discussed above, by reducing the thickness of wafers and improving the processes of recycling any scrap materials.