

# Inorganic Photovoltaic Solar Cells: Silicon and Beyond

by Meng Tao

Photovoltaic solar cells tap into sunlight—the most abundant renewable energy source on the Earth—for electricity. Our planet receives  $\sim 1.2 \times 10^{17}$  W of solar power, while the rate of current worldwide energy consumption is  $\sim 10,000$  times smaller at  $\sim 1.3 \times 10^{13}$  W.<sup>1</sup> This means that the Earth receives more solar energy in an hour than the total energy it consumes in an entire year. Solar energy alone has the capacity to meet all the planet's energy needs for the foreseeable future. No other renewable energy sources have such a capacity, so they can only serve as auxiliary energy sources in our future energy mix. Other renewable energy sources include wind, hydroelectric energy, biomass, ocean currents, tides and waves, and geothermal energy. It is interesting that many of the other

renewable energy sources originate from solar energy, except perhaps ocean tides and geothermal energy. The land requirement for solar cells is minimal. Covering 0.16% of the Earth's surface with 10% efficient cells would provide  $\sim 2 \times 10^{13}$  W of electricity, more than the current total energy demand of the planet.<sup>1</sup>

In sharp contrast to the huge amount of solar energy we receive, solar cells account for only 0.014% of the electricity the U.S. consumed in 2005, according to the U.S. Department of Energy.<sup>2</sup> Worldwide, the contribution of solar electricity is higher due to many installed solar modules in Europe and Japan, but still an insignificant number. If by 2050 solar cells contribute to just 10% of the electricity we consume, the U.S. solar cell industry will have to grow  $\sim 1,000$ -fold in size, assuming that

our demand for electricity will double by 2050. Both the potential and gap in solar energy utilization by solar cells are enormous.

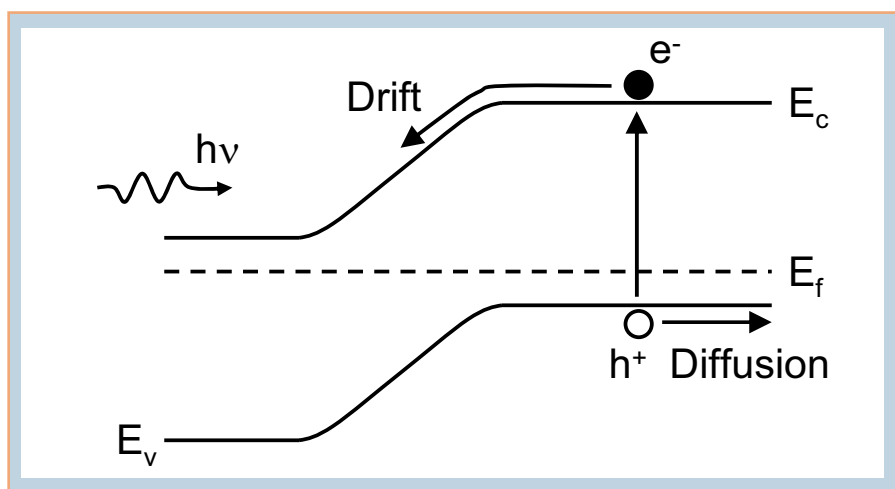
It should be noted that solar cells are just one of the several approaches for solar energy utilization. They convert solar energy into one of the most popular forms of energy in our life: electricity. The other popular form of energy in our life is gasoline as a fuel. Solar-to-chemical conversion through artificial photosynthesis is being developed to produce alternative fuels. Solar energy can also be converted into thermal energy by solar water heaters and into concentrated thermal energy for electricity generation.

## Photovoltaic Solar Cells

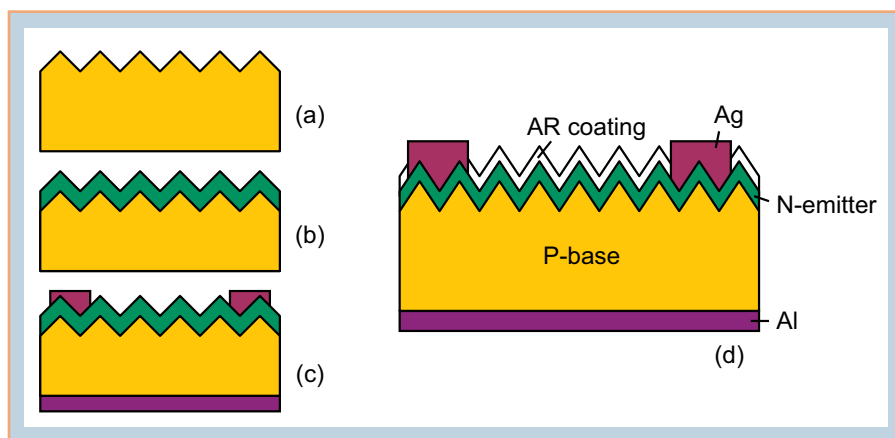
The photovoltaic effect, *i.e.* light-induced voltage, was discovered in 1839 by E. Becquerel when he shed light onto an AgCl electrode in an electrolyte solution.<sup>3</sup> C. Fritts demonstrated the first solid-state solar cell in 1883 by depositing a thin layer of Au on Se semiconductor.<sup>4</sup> The semiconductor served as the light absorber to convert photons into electron-hole pairs, and the internal electric field in the Au/Se Schottky junction separated the photo-excited charge carriers. The two fundamental processes, namely light absorption and charge separation, are still the basis in all inorganic solar cells today. Modern solar cells were patented in 1946 by Ohl<sup>5</sup> and demonstrated in 1954 by Chapin, Fuller, and Pearson at Bell Laboratories.<sup>6</sup> Their cell employed a single-crystal Si (sc-Si) wafer for light absorption and a p-n junction for charge separation, with an efficiency of  $\sim 5\%$ .

Figure 1 illustrates the principle of this cell. Photon absorption is throughout the wafer and extends outside the depletion region. Therefore, charge separation involves diffusion of photo-excited charge carriers toward the depletion region. This makes the quality of the entire wafer critical in terms of minority carrier lifetime and carrier mobility for high efficiency. In comparison, it is the quality of the *surface* region which matters most in CMOS devices, since CMOS operation takes place within a thin layer ( $< 100$  nm) of the wafer surface.

Although the efficiency of solar cells has been improving steadily since 1954, the majority of today's commercial solar cells still resemble the Bell Laboratories cell, *i.e.*, they utilize a Si wafer in either single-crystal or polycrystalline form for light absorption and a p-n junction for charge separation. Figure 2 shows



**Fig. 1.** Principle of wafer-Si solar cells: photon absorption is throughout the wafer and charge separation often involves diffusion of photo-excited charge carriers.



**Fig. 2.** Cross section (d) and fabrication process of single-crystal Si solar cells: (a) surface texturing, (b) n-emitter diffusion, (c) metallization, and (d) antireflection coating.

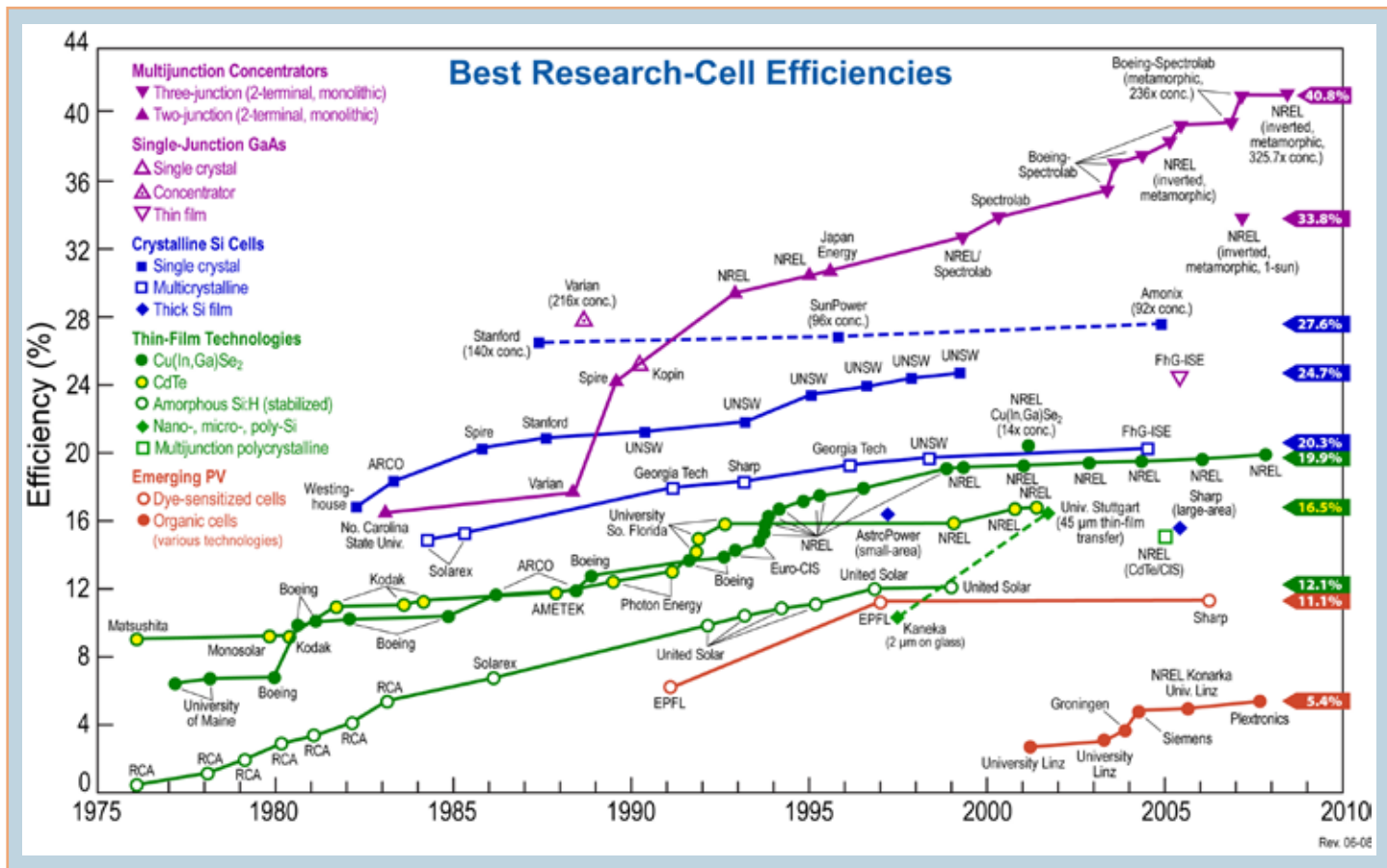


Fig. 3. Evolution of best laboratory efficiency for different solar cell technologies. (Source: National Renewable Energy Laboratory, 2008)

schematically the cross section and fabrication process of a common structure for sc-Si cells. It starts with a p-type Si(100) wafer with resistivity of  $\sim 1 \Omega\text{-cm}$ . The wafer is first etched in either NaOH or KOH to form microscale pyramids with (111) facets on the surface. The textured surface reduces sunlight reflection, since reflected light from a pyramid often strikes another pyramid, thus a second chance of incidence. A p-n junction is formed by diffusing an n-type dopant, often P, into the front side of the wafer for a typical depth of  $\sim 0.5 \mu\text{m}$ . The backside electrical contact is formed by reacting a screen-printed Al film with the wafer to form an AlSi compound. The front finger contact is also screen-printed with an Ag paste. The typical width of the contact fingers is  $\sim 200 \mu\text{m}$  and the separation between two fingers is  $\sim 3 \text{mm}$ , for a balance between minimum resistance and minimum light shadowing. Finally a transparent material, often  $\text{SiN}_x$ , is deposited on the wafer as an antireflection coating by plasma-enhanced chemical vapor deposition (PECVD).

Figure 3 shows the evolution of efficiency for various solar cell technologies over the last three decades. The efficiency of sc-Si cells has reached 24.7%, while that of polycrystalline Si (poly-Si) cells is 20.3%. The record efficiency for all solar cell technologies is held at 40.8% by a so-called tandem cell. This cell stacks three p-n junctions made of  $\text{Ga}_x\text{In}_{1-x}\text{As}$  or  $\text{Ga}_x\text{In}_{1-y}\text{P}$  with

different compositions. Each junction has a different band gap and is responsible for light absorption in a certain portion of the solar spectrum. The efficiency is measured with a concentrator under 326 Suns. Under one Sun, the efficiency of this triple-junction cell is 33.8%. Besides wafer Si, several thin-film solar cell technologies have been commercialized, including Si in either amorphous (a-Si) or microcrystalline ( $\mu\text{-Si}$ ) form and metal chalcogenides (CdTe and  $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$  (CIGS)). Their record efficiencies range between 12% and 20%. While the progress in efficiencies of these laboratory-size solar cells has been remarkable, commercial-size cells and modules are typically one-half to two-thirds of these efficiencies. Closing the

efficiency gap is the subject of ongoing research, especially by the solar cell industry.

This article focuses on wafer-Si solar cells, the so-called first-generation solar cells, which dominate the current solar cell market. It also speculates two directions to pursue for future solar cells. For more details on thin-film based second-generation CIGS solar cells on a-Si,  $\mu\text{-Si}$ , CdTe, and CIGS, the reader is referred to *MRS Bulletin*, Vol. 32, No. 3 (March 2007).

### Solar Cell Industry

The current solar cell industry is dominated by Si with nearly 90% of the market. Figure 4 shows the 2007 market shares by different solar cell

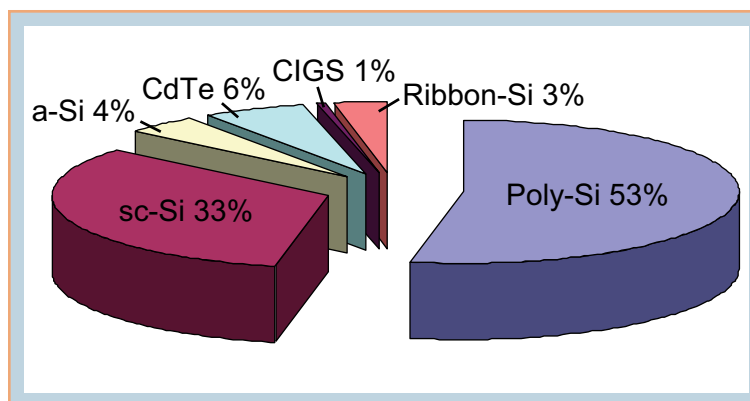


Fig. 4. Market shares by different solar cell technologies in 2007. (Courtesy of Paula Mints, Navigant Consulting PV Services Program)

technologies, with poly-Si leading the way at 53%, followed by sc-Si at 33%. All the thin-film technologies combined have 11% of the market. A noticeable trend in the solar industry over the last ten years is that the market share for poly-Si cells has expanded significantly, cutting into the market shares of a-Si as well as sc-Si cells.<sup>7</sup> With the shortage of Si material in recent years, the market shares of CdTe and CIGS are also expanding.

There are several technical and economic factors leading to the dominance of Si in the solar cell industry. Among them, the technical know-how developed by the semiconductor industry by the 1970s, when the solar industry was born, undoubtedly contributed to the dominance of Si. By the late 1950s, the semiconductor industry had already made Si the material of choice. Materials science, device physics, and fabrication technology had all been well established for Si by the '70s. In those days, there was little difference between the two industries in terms of materials, processes, and equipment. However, the solar industry quickly recognized that the economics works differently in the two industries, and it started to take on its own path.

A fundamental difference between the two industries is Moore's law, which underlines the phenomenal growth of the semiconductor industry in the last four decades but does not apply to the solar industry. (Ed. Note: See *Interface*, the spring 2005, spring 2007, and fall 2007 issues for further discussion on the impact of Moore's law.) By shrinking the transistor size, the cost of integrated circuits has been decreasing exponentially over time and their performance improving exponentially. These low-cost, high-performance Si chips have now penetrated into every household in the U.S. for computers, telecommunications, and consumer electronics. On the other hand, sunlight is a low-intensity energy source up to  $\sim 1,000 \text{ W/m}^2$ . To generate more solar electricity, more solar cells are needed. Over the last three decades, the solar industry has relied on two approaches to reduce the cost, *i.e.*, production scale-up and process improvement. The result is a more-or-less linear, instead of exponential, reduction in cost over time (see Fig. 5). The recent rise in cost is due to the shortage of Si material.

Another difference between the two industries is the variety of materials, processes, and devices, which are competing for the solar cell market, versus the CMOS-dominant semiconductor industry. The CMOS technology was developed in the 1970s and quickly overtook the semiconductor industry, primarily for its low power. In the solar industry, several technologies coexist. Each of these

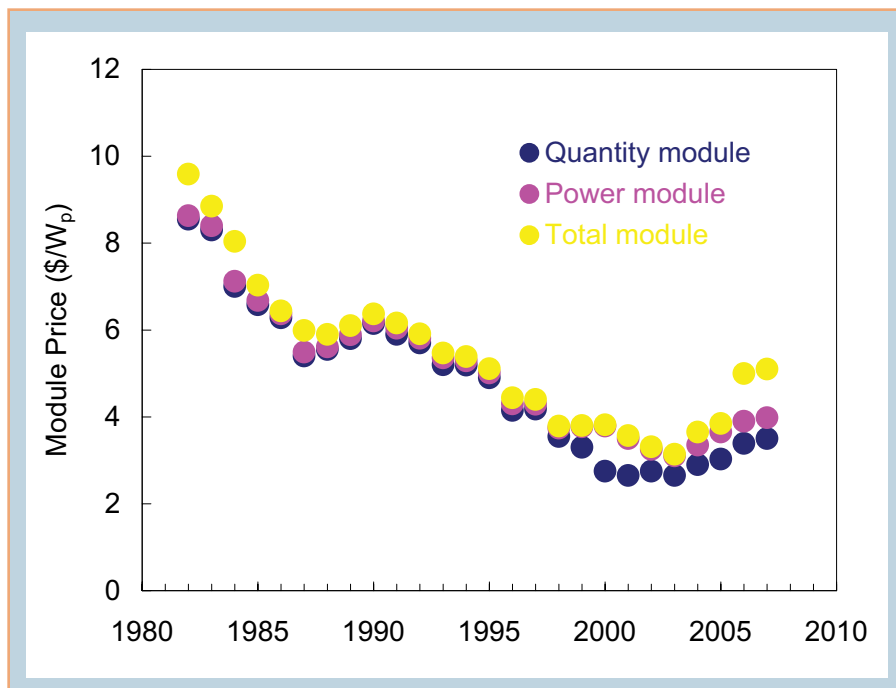


Fig. 5. Trend in solar module price, 1982-2007. (Courtesy of Paula Mints, Navigant Consulting PV Services Program)

technologies has its own pros and cons. For example, the device in Fig. 2 is just one of the several structures for commercial sc-Si cells. Other structures include SunPower's back-contact cells with a record efficiency for commercial single-junction cells at  $\sim 23\%$ <sup>8</sup> and Sanyo's sc-Si/a-Si heterojunction cells with a record open-circuit voltage of  $\sim 0.73 \text{ V}$  for Si cells.<sup>9</sup> This divergence presents an interesting question, *i.e.*, is there a most cost-effective way to make terrestrial solar cells?

The price of solar modules is  $\sim \$3.50/W_p$  and that of installed solar systems  $\sim \$7/W_p$  today ( $W_p$  stands for power under peak solar intensity), which translates into  $\$0.25 - 0.65/\text{kWh}$ .<sup>10</sup> This price is  $\sim 5$  times higher than electricity from fossil fuels. Although the public may be forced to accept high-cost solar electricity when other energy sources become expensive or scarce, one can hardly underestimate the profound impact of a low-cost solar cell technology. The growth of the industry has been rapid at  $\sim 40\%$  per year and becomes exponential in recent years due to the hikes in oil price. In 2007, the worldwide solar industry reached  $3.4 \times 10^9 W_p$  in production and  $\$17\text{B}$  in revenue.<sup>11</sup>

The low-intensity solar energy has several consequences for the solar cell industry. For a family consuming 20 kWh/day, it is estimated that a minimum of  $\sim 30 \text{ m}^2$  solar cells is needed assuming 15% efficiency,  $1,000 \text{ W/m}^2$  solar intensity, and five hours of daily solar radiation. This is equivalent of  $\sim 1,000$  8-in Si wafers assuming 100% wafer usage. In fact, the actual number of 8-in wafers for such a family is  $\sim 1,200$  since

circular Si wafers are typically cut into a quasi-square shape for close packing in solar modules. Therefore, the amount of Si material required for such a family is  $\sim 10,000$  times more than that for a computer. If the same Si wafers for the semiconductor industry were used for solar cells, the wafer cost ( $\sim \$100/\text{wafer}$ ) would be prohibitively high. Even with low-cost scrap Si material from the semiconductor industry, material cost is still the largest contributor to the overall cost of wafer-Si cells at  $\sim 50\%$  (see Fig. 6), and that supply of Si is extremely limited. In comparison, the cost of Si material is trivial for the semiconductor industry. The large quantity of Si material required by solar cells also creates a shortage of Si material whenever the solar industry accelerates.

### Figure of Merit

Efficiency and cost are the two often-cited parameters for terrestrial solar cells. The bottleneck for solar electricity to become a household energy source is the cost. Efficiency improvement is often accompanied with additional cost, so it has to be done in a cost-effective manner. This suggests that a better figure of merit for terrestrial solar cells is the efficiency/cost ratio in  $\%W_p/\$$ . It reveals the effectiveness of our investment, *i.e.*, for each dollar we spend, how much do we gain in the product of efficiency and power. It may be used to judge any solar cell technology candidate for its commercial potential, as illustrated later.

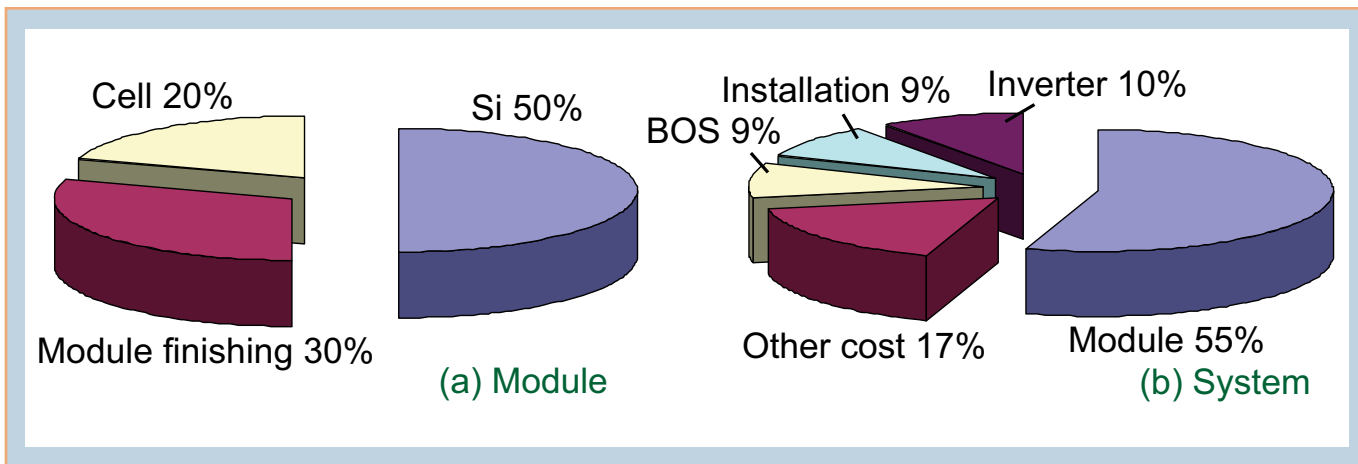
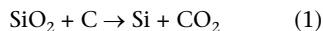


Fig. 6. Cost breakdown for solar modules and systems. (Source: Harriet Kung, U.S. Department of Energy, 2005)

### The Cost

It is intriguing to look at the current industrial process from quartz to Si wafers (see Fig. 7),<sup>12</sup> which provides some insight into the high cost of wafer-Si cells. Quartz is favored over sand in Si wafer production for its high purity. It is reduced to Si in an electric-arc furnace with charcoal at  $\sim 1,900^\circ\text{C}$ :



The Si produced is called metallurgical-grade (MG) Si and is only  $\sim 99\%$  pure, insufficient for electronic devices including solar cells. The energy input for this process is  $\sim 50$  kWh/kg. The current worldwide production of MG-Si is  $\sim 600,000$  tons/year, which releases several million tons of greenhouse gas,  $\text{CO}_2$ , into the atmosphere.

A small fraction of the 600,000-ton MG-Si,  $\sim 5\%$ , is purified to produce electronic-grade (EG) Si for the semiconductor industry. The required

impurity level in EG-Si is below 0.1 ppm or the purity of EG-Si is above 99.99999% (seven nines). For solar-grade (SG) Si, the required impurity level is below  $\sim 1$  ppm or six nines (99.9999%).<sup>7</sup> MG-Si is reacted with HCl to form  $\text{SiHCl}_3$ , which is purified by multiple distillation. The corrosive  $\text{SiHCl}_3$  attacks stainless steel, resulting in frequent replacement of the equipment. The purified  $\text{SiHCl}_3$  is then reduced by  $\text{H}_2$  to produce high-purity poly-Si in the so-called Siemens process. The reaction takes place on a high-purity Si rod which is maintained at  $\sim 1,150^\circ\text{C}$  by passing an electrical current through it. This turns out to be a very energy-intensive process at  $\sim 200$  kWh/kg.

The high-purity poly-Si produced is crystallized into single-crystal ingots by the Czochralski process, in which poly-Si is first melt at  $1,414^\circ\text{C}$  in a high-purity quartz crucible. A Si seed crystal is brought into contact with the melt and then pulled out slowly. With the

temperature tightly controlled, melt Si crystallizes on the seed. The seed is rotated, resulting in a cylindrical ingot of sc-Si. A controlled amount of B or P is usually added to the crucible to dope the ingot p- or n-type to a specific range of resistivity. The energy input for the Czochralski process is  $\sim 100$  kWh/kg.

The cylindrical Si ingot is usually cut into a quasi-square shape, resulting in  $\sim 25\%$  material loss. The square ingot is then sliced into wafers. The slicing is very slow, taking many hours to cut through an ingot. Even with the multiple-wire saw, which has a much higher throughput than the inner-diameter saw used for the semiconductor industry, slicing is one of the most costly steps in Si wafer production. There is also a significant material loss as saw dust during slicing, up to  $\sim 30\%$ . Finally, the Si wafers are polished to remove any damage by the sawing step and cleaned for cell fabrication.

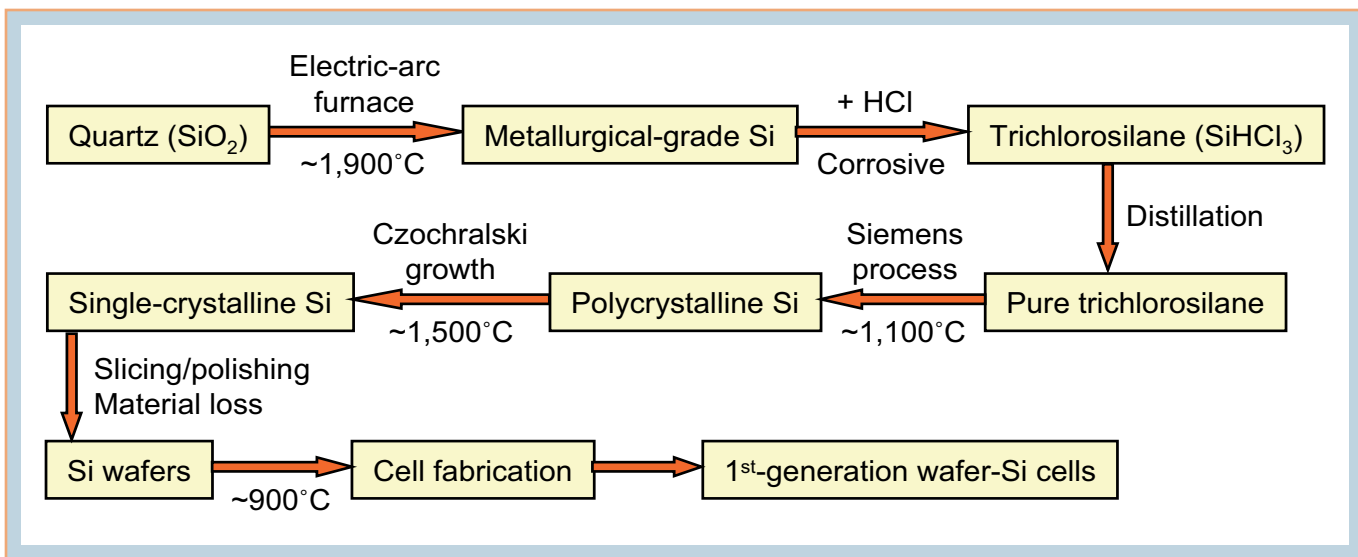


Fig. 7. Industrial process from quartz to single-crystal Si cells. The energy input for electric-arc furnace, Siemens process, and Czochralski growth is  $\sim 50$ ,  $\sim 200$ , and  $\sim 100$  kWh/kg, respectively.

The electricity consumption for sc-Si wafers is, taking into account of material loss during slicing,  $\sim 700$  kWh/kg. If sc-Si cells are deployed at  $5 \times 10^{11}$   $W_p$  a year which can generate  $\sim 4\%$  of the 2005 worldwide electricity production,<sup>2</sup> the amount of sc-Si wafers required is  $\sim 2,350,000$  tons/year. This amount of sc-Si wafers would require  $\sim 1.6 \times 10^{12}$  kWh or  $\sim 10\%$  of the world electricity production. This is a fundamental limit for wafer-Si cells to make a noticeable contribution to electricity generation, although it has not been reached due to the small scale of today's solar industry. The discussion also brings out an important concept in the solar industry: the energy payback time, which is the time that a solar cell takes to produce the same amount of energy for fabricating it. For sc-Si cells, it is  $\sim 3$  years.

To reduce the cost and energy input of solar cells, the solar industry has developed some solar-specific materials, processes, and equipment. One example is directional solidification for growth of poly-Si ingots, which requires  $\sim 12$  kWh/kg of electricity versus  $\sim 100$  kWh/kg for the Czochralski process,<sup>12</sup> a  $\sim 88\%$  saving in electricity. This illustrates the cost-driven nature of the solar industry. The efficiency of poly-Si cells is lower than that of sc-Si cells, but the industry is willing to trade a little efficiency for a large return in cost, thus a better efficiency/cost ratio. Another example is screen printing for metallization, which prints Al and Ag pastes into various shapes for electrical contacts. In comparison, metallization in most record-efficiency cells is performed by vacuum-based metallization, e.g., evaporation or sputtering, and photolithographic patterning. Again, the industry trades efficiency for cost.

## Future Directions

The lack of a "perfect" semiconductor or semiconductors for terrestrial solar cells has been a fundamental limit to an exponential expansion of the solar cell industry. These cells need to be deployed on a scale of  $\sim 10^{12}$  W to make a meaningful impact on our energy infrastructure. They need to go on rooftops, windows, highways, and large-scale solar farms. The widespread deployment of solar cells requires many desirable properties for the semiconductor(s) in the cells. Table I lists some of these desired properties. Roughly speaking, requirements 1 through 5 are for low cost and 6 through 10 for high efficiency. Although solar cells have been demonstrated for many inorganic semiconductor materials, none of them meets all the requirements in Table I. This underlines both the challenges and opportunities for future generations of researchers.

As outlined in Table I, Si is not at all a bad material for solar cells. It is abundant and non-toxic, but it is expensive with a non-optimum band gap. The 1.1-eV band gap of Si is smaller than the optimum band gap for single-junction cells,  $\sim 1.4$  eV.<sup>13</sup> However, the sophistication of the Si technology has made up for this non-optimal band gap handicap. Single-crystal Si holds the efficiency record for single-junction cells at  $\sim 25\%$ . If the cost and energy input of wafer-Si cells can be significantly reduced, Si may remain as the dominant solar cell material for the foreseeable future.

One approach to reduce the cost is to reduce the amount of Si material used in wafer-Si cells. This can be realized by: (a) reducing the thickness of the Si wafer and (b) reducing the material loss during ingot slicing. The current wafer thickness is  $\sim 200$   $\mu\text{m}$  and some predict that it will reach 100  $\mu\text{m}$  or less in the next ten years. Advanced wafer handling capabilities need to be developed for these fragilely-thin wafers.

Recent work from Japan and Norway suggests the potential of electrochemistry for much more energy-efficient routes to SG-Si.<sup>14</sup> In principle, each electron transfer in an electrochemical process leads to a chemical reaction. Therefore, the internal quantum efficiency in an electrochemical process is 100%, although resistive loss in external circuits brings down the overall efficiency. In contrast, the current industrial process from quartz to Si wafers relies heavily on thermal processes. In a thermal process, a large chunk of material is heated to a high temperature to activate a tiny fraction of it for reaction. This activated fraction is proportional to  $\exp(-E_a/RT)$ , where  $E_a$  is the activation energy for the chemical reaction. Therefore, electrochemistry might be the key to significantly reduce the electricity input in Si wafer production.

Alternatively, new materials may replace Si for terrestrial solar cells in the future. CdTe and CIGS are examples of this approach. Although these materials require lower energy input than Si and their market shares are expanding, they suffer a different set of problems. In is expensive and Te is scarce, if they are deployed at the  $10^{12}$  W scale. Therefore, none of the commercial solar cell materials satisfies all the requirements in Table I. After five decades since the Bell Laboratories Si cell and half-a-dozen successful solar cell technologies, the author believes that a broad search for the "perfect" material(s) for terrestrial solar cells is still needed.

A root cause for the high cost of wafer-Si cells, from a materials scientist's perspective, is the directionality and strength of the covalent bond in Si. It makes Si hard to cut through

and requires high temperatures to process Si. It derails our attempts to synthesize Si by low-cost methods. Solution synthesis of Si is difficult and a-Si by PECVD possesses much poorer electrical properties than its crystalline counterparts. For example, the carrier mobility in a-Si is often below  $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , versus  $450 - 1,500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  in sc-Si. This is because the bond length and angle are both rigidly fixed in Si. Any atomic misalignment leads to a strained bond or a dangling bond, both of which translate to electronic defects in the crystal. In low-cost Si, the density of these defects is so high that the material becomes structurally amorphous and the electrical properties deteriorate dramatically.

Of the two types of chemical bonds in inorganic semiconductors: covalent and ionic, the author believes that ionically-bonded semiconductors are worth our attention. The ionic bond is non-directional, i.e., the bond angle is not rigidly fixed due to the Columbic nature of the bond. Metal chalcogenides including oxides, sulfides, and selenides belong to this category. CdTe and CIGS also belong to this category, but our search should focus on abundant, low-cost, and non-toxic metal chalcogenides. The flexibility of the ionic bond allows small atomic misalignment to be accommodated in the crystal without introducing an electronic defect. The implication is significant. Many metal chalcogenides can be synthesized into polycrystalline forms by various low-cost methods with excellent electrical properties. In fact, solution-fabricated CIGS cells are being commercialized with over 10% efficiency.<sup>15,16</sup> Recent progress in solution fabrication of inorganic cells includes electrochemical deposition of CIGS,<sup>17</sup> spray deposition of CIGS,<sup>18</sup> electrical contacts by direct writing,<sup>19</sup> and surface textures by solution coating.<sup>20</sup>

Tandem cells are the only proven approach to high efficiency of 30% and more. One may speculate that solution-fabricated tandem cells of high efficiency will be realized in ionically-bonded semiconductors, but this has yet to be demonstrated. This approach requires the identification of several ionically-bonded semiconductors with suitable band gaps. The optimum band gaps for a tandem cell can be determined by matching the photon flux for each junction. For a triple-junction cell, one combination of optimum band gaps is  $\sim 0.8$ ,  $\sim 1.3$ , and  $\sim 1.8$  eV. The electrical properties of these semiconductors have to be well controlled: carrier mobility, minority carrier lifetime, conduction type, and resistivity. These are the same problems we solved for Si in the 1950s and '60s. In this sense, solution fabrication of tandem cells is still at its infancy with an additional difficulty, i.e., all the problems are preferably solved in solution.

## Summary

Wafer-Si solar cells dominate today's solar cell industry with nearly 90% of the market. The bottleneck for solar electricity to become a household energy source is cost. This article has examined several root causes for the high cost of solar electricity including: (a) the low intensity of solar radiation and (b) the directional and strong covalent bond in Si. The former requires a large quantity of Si material to generate a noticeable amount of electricity. The latter makes Si hard to process and wafer-Si cells become costly and energy-intensive. The article also discusses a fundamental limit for terawatt-scale deployment of wafer-Si cells, *i.e.*, the huge energy input for wafer-Si cells. Finally, the article speculates two directions to pursue for future solar cells. One is low-cost and energy-efficient fabrication of wafer-Si cells. Another direction is new materials, which allow solution fabrication of tandem cells to achieve a much better efficiency/cost ratio than wafer-Si cells. Ionically-bonded semiconductors are suggested for this purpose, and desired properties for these to-be-identified semiconductors are outlined.

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**Table I. Material requirements for terrestrial solar cells.**

Material Requirement	Material Meeting Requirement
1. Abundant material	Si
2. Low-cost material	CdTe, CIGS
3. Low-cost synthesis	CdTe, CIGS
4. Non-toxic material	Si, CIGS
5. Stable material	Si, III-V, CdTe, CIGS
6. High mobility	Si, III-V, CdTe, CIGS
7. High carrier lifetime	Si, III-V
8. Suitable band gap	III-V, CdTe, CIGS
9. Control of conduction type	Si, III-V, CdTe, CIGS
10. Control of resistivity	Si, III-V, CdTe, CIGS