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Photovoltaic materials and crystal growth research and development in the Gigawatt era

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A B S T R A C T

The photovoltaic (PV) industry has recently undergone a period of oversupply and plunging prices which has imposed a harsh reevaluation of criteria for viability. The background history leading up to the current PV technology situation is presented and discussed in terms of the PV learning curve (PV module selling price as a function of amount produced). The effects of the past and recent learning curve fluctuations and their technological causes on various PV material crystal growth approaches are described. Some crystal growth research and development (R&D) needs for future viability are discussed.

1. Introduction

Silicon has historically been the work horse material for PV energy systems. Its supply, associated cost, and advances in the efficiency of silicon solar cells have been the drivers for R&D trends in PV materials. For example, when Si supply is low and prices are high, interest is spurred in ribbon and sheet silicon crystal growth, wafering technology, and efficiency advancement. Alternate ways of making pure silicon feedstock are explored (e.g. upgraded metallurgical grade or MG silicon). Alternative thin film PV materials such as CdTe, $\mathrm{CuIn_xGa_{1-x}Se_2}$, and amorphous silicon receive increased interest. When high-purity silicon feedstock supply is plentiful and prices are low, these subjects are no longer of high interest. In addition, low Si prices can contribute to a glut or oversupply of PV modules and lead to pressure on suppliers to lower their manufacturing costs and increase their module efficiencies in order to remain competitive in a cut-throat market. This is the situation the PV industry is facing at the present time. PV module prices have recently fallen much faster than historically expected, and this is demanding new R&D focus directions for viability. A convenient framework for discussing these past and present trends in PV materials crystal growth R&D is a construct called a “learning curve” which plots the change in PV module cost as a function of amount of material produced. The learning curve framework for interpreting PV technology advances and making projections for the future course of the industry was presented by Swanson in 2006 [1]. The learning curve for the PV industry is shown in Fig. 1, and plots module selling price in 2010 \$/Watt vs. cumulative megawatts (MW) of modules produced.

2. Historical background

The two deviations from the regression line of the learning curve of Fig. 1 labeled “Silicon shortage” and “Excess capacity” are the main causes for shifts in PV materials crystal growth R&D emphasis in the past decade. Another plot, shown in Fig. 2, complements Fig. 1 as a basis for discussing these shifts. It shows the selling price of high purity polycrystalline silicon feedstock as afunction of time in years.

In the 1990s the main use for high purity silicon feedstock was in Czochralski (CZ) growth for the integrated circuit (IC) industry. The price was typically in the range \$60/kg–\$90/kg. The technology bubble of the 1990s led to an increased demand for polysilicon, and suppliers accordingly built increased production capacity. When the technology bubble burst in the late 1990s, the suppliers were left with excess inventory and production capacity. Although demand for polysilicon in the integrated circuit industry dipped, the PV industry had been growing strongly at a rate $>40\%$/year and took advantage of the lower price ($\sim$\$30/kg). By about 2003, the crossover point was reached at which more silicon was being used for PV than for ICs, and the rate of growth was still in the 40%/year range. The earlier excess polysilicon capacity was soon consumed by PV applications. It would have been appropriate for polysilicon suppliers to recognize the rapid PV growth in the years 2000–2003 and beyond, and expand capacity accordingly. However, because of their bad experience with the bursting of the dot com technology bubble in the late 1990s they were reluctant to do so. Silicon supply became constricted and prices rose dramatically, peaking at about \$475/kg in 2007, and the price of PV modules deviated strongly upward from the mean PV learning curve in the

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years 2004–2008. The influence of this deviation in the learning curve labeled "Silicon shortage" upon PV materials crystal growth R&D will be discussed in the subsequent section.

The major polysilicon suppliers did eventually realize that the PV demand for silicon was substantial and sustained. They began expanding capacity but because of the long lead times needed to get new production facilities built and running, the increased supply began to be significant only in about 2008. While there had been a few major silicon suppliers in the past, the high polysilicon prices and growth opportunities for silicon in PV had also lured many other polysilicon producers to enter the industry. The polysilicon supply rose to 85,000 metric tons in 2009 and increased four-fold to the current output (in 2013) of about 337,000 metric tons. The huge increase in polysilicon supply and rapidly plunging price, coupled with various government's political policies which reduced PV demand, led to a corresponding glut of silicon PV modules in the market and module prices fell well below the mean learning curve. A long range goal in the PV industry had been to achieve module selling prices less than $1/W. Exceeding this target early (~$0.85/W) in 2012 and the associated "Excess capacity" region of the learning curve in Fig. 1 have led to a shakeout in the industry with many companies and technology approaches failing. The effect of the "Excess capacity" region of the learning curve on PV materials crystal growth R&D will also be discussed in the following section.

3. Effect of learning curve anomalies on PV crystal growth and materials technology

Some of the effects of the 2003–2008 "Silicon shortage" and the 2011-to-present "Excess capacity" regions of the Fig. 1 learning curve can be discussed in the context of the silicon IC industry process flow chart of Fig. 3. In brief, sand or quartzite is reduced with coke in an arc furnace, creating low-purity MG silicon which is reacted with HCl to form chlorosilanes. After fractional distillation (the key purification step) high purity $SiHCl_3$ is obtained and then reduced to high purity polysilicon by chemical vapor deposition CVD with H_2 on hot thin-rod substrates. This is called the Siemens process. Alternatively SiH_4 can be used in a fluidized bed (FB) CVD process to obtain high-purity polysilicon beads. Dislocation-free CZ crystals are grown from the polysilicon, wafered, and polished for device fabrication.

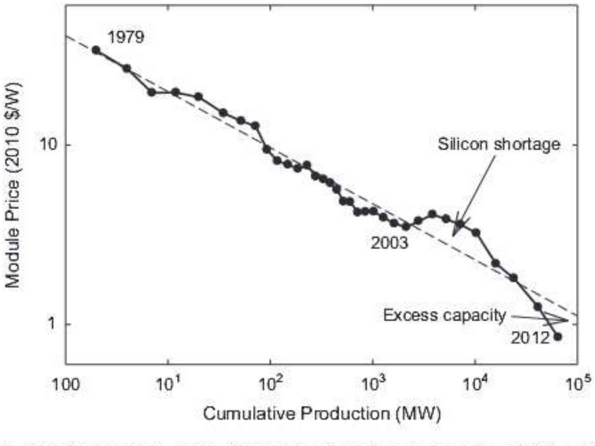

Fig. 1. The PV learning curve illustrating the change in price of PV modules (in 2010 $) as a function of cumulative module production (in MW).

3.1. Changes in focus of R&D on silicon feedstock processes

3.1.1. Up-graded metallurgical-grade silicon feedstock

In the "Silicon shortage" period, a number of efforts were initiated on up-graded MG silicon. These typically entailed using higher purity quartzite and carbon-based starting materials in the arc furnace process followed by several directional solidification steps to take advantage of the low effective segregation coefficient k_e of metallic impurities in silicon. The main dopant impurities, B and P, however have k_e much closer to 1 and other means are necessary to remove them. Slagging, holding the melt under vacuum for prolonged periods, and bubbling gases through the melt are some of the techniques employed. Purity levels in the five 9s range could be achieved [2], generally not adequate for high performance silicon solar cells when used as a sole feedstock source, but sufficient for blending with higher purity polysilicon. With the recent drastic drop in price of high-purity polysilicon, and because of the higher solar cell efficiencies that can be obtained with it, the efforts on up-graded MG Si have largely ceased. There is still some application for it in the lower-performing multicrystalline ingot growth.

3.1.2. Conventional high-purity CVD silicon feedstock

Because the recent selling price of polysilicon is near or below cost for many suppliers, there has been a major shake out of companies. For survival, the remaining ones need to focus on the primary cost drivers, including reactor design, scale of operation, energy utilization, and throughput, as well as sourcing and recycling of process gases.

The FB approach for making bead-shape silicon feedstock became more prominent when polysilicon prices reached high levels. It had been developed in the mid-1970s but received increased focus after 2003. It has advantages of not needing a thin rod substrate, lower energy costs, and being a semi-continuous process. It is generally conducted with SiH_4 decomposition onto granular "seeds", but some efforts were initiated with $SiHCl_3$ source material as well. Because profit margins are currently so low for polysilicon, the FB approach continues to receive emphasis. A focus is on finding a good balance between cost reduction and purity. Some technology issues faced by FB Si include

- new rapid, low cost, and meaningful means of checking purity are needed;
- materials handling is more difficult due to bead size and electrostatics;
- the form factor for crucible loading is not ideal for beads alone;

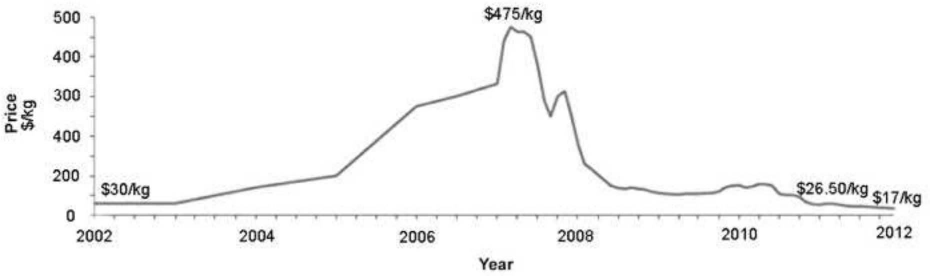

Fig. 2. The historical price of high-purity polycrystalline silicon.

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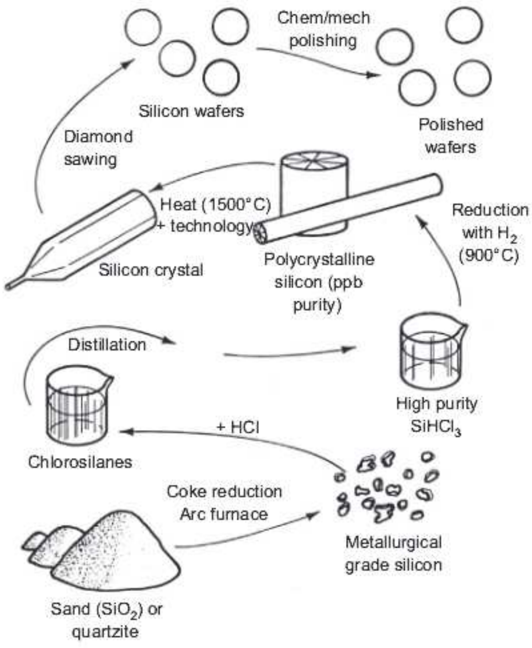

Fig. 3. The silicon process flow chart.

- silane (SiH_4) is highly preferred over $SiHCl_3$ for FB, but is more hazardous.

Some alternatives to the Siemens and FB processes were also explored in the "Silicon shortage" period. One example is the use of atmospheric pressure iodine vapor transport disproportionation reaction [3].

3.2. Changes in focus of R&D to reduce utilization of silicon

With silicon prices high and supply constrained, much focus had been placed on alternative growth methods that could avoid the silicon wafering process in which half the silicon is lost as saw kerf. Growth of silicon in the form of ribbons or sheets does not require wafering. A dozen approaches have been tried for such growth over many decades. The main four that were active during the "Silicon shortage" are shown in Table 1. They are silicon dendritic web growth or WEB, first reported in 1965 [4]; silicon edge-defined film-fed growth EFG, first reported in 1972 [5]; silicon edge-supported pulling ESP or string ribbon growth, first reported in 1980 [6]; and silicon ribbon growth on a substrate RGS first reported in 1994 [7]. These methods were attractive in the "Silicon shortage" period because they used approximately half as much silicon as do ingot methods and avoided the wafering process. They were also perceived to be fast methods because the pulling speed was on the order of 10 times that of CZ crystals (much higher, though, for RGS). However, the actual throughput, when compared to ingot growth with concomitant wire sawing is much lower in most cases. This is shown in Table 2, where the comparisons are made with CZ growth, float zone FZ growth, directional solidification DS of block-shaped multicrystalline ingots, and multicrystalline electromagnetic casting EMC.

The ribbon and sheet growth methods, once in vogue when silicon was expensive and scarce, lack the throughput and PV efficiency (due to grain size and impurity content) to compete against large silicon ingots in the present era of abundant, low-cost, and high purity silicon. Of the 27 GW of PV material produced in 2011, 57% was grown by the DS method, 31% by dislocation-free single crystal CZ growth, and the remaining 12% by ribbon silicon, CdTe thin films, $CuInGaSe_2$ thin films, and amorphous silicon thin films combined.

The other way in which silicon utilization was minimized in the "Silicon shortage" period is by advancements in multi-wafer wire sawing of Si ingots. This is ongoing because the benefits are significant even in the present "Excess capacity" era. Currently, silicon carbide slurry multi-wafer sawing achieves 180 μm thick 15 cm wide wafers with a wire diameter of 120 μm. Efforts are also underway to use diamond-coated wires.

3.3. Changes in focus of R&D on alternatives to crystalline silicon for PV

Because crystalline silicon is an indirect bandgap semiconductor, a relatively large thickness is required for light absorption (50 μm for 90% absorption and 100 μm for 95% absorption). So efforts have long been underway to develop thin film alternative semiconductors with better absorption coefficients for PV. The primary ones are amorphous silicon (α-Si), $CuIn_xGa_{1-x}Se_2$, and CdTe. In the "Silicon shortage" era, these were aggressively pursued and perceived as inevitable eventual replacements for silicon. Sophisticated multi-junction solar cells based on epitaxial (EPI) growth of III–V were also aggressively developed on the premise that their higher efficiencies would offset the higher costs of deposition materials, substrates and concentrator systems. The long range goal was to achieve PV modules at $<\$1/W$ selling price.

When silicon PV modules, because of excess polysilicon capacity, low polysilicon prices, and excess module inventory, reached selling prices below $1/W ($0.85/W in 2012) much earlier than expected from the mean learning curve, the thin film approaches other than CdTe were not able to compete. And even the major CdTe PV module manufacturer is initiating efforts in crystalline Si modules.

Fundamental issues facing alternate PV materials are abundance in the earth's crust and toxicity level (see Table 3). These are impediments to large scale deployment. As a case in point, because it is scarce, Te prices have recently risen by a factor of 5. It is largely obtained as a byproduct of copper smelting, and expansion is thus not easily accomplished although mining efforts specifically for Te are in progress. If all the Te available for PV manufacturing in 2012 were used to make PV modules, only 10 GW could have been produced.

Other issues facing alternate PV materials are meeting Si PV module efficiencies at a lower cost, in the case of thin films, and substrate and material costs (especially metal–organic precursors), throughput, and concentrator system costs in the case of III–V.

4. Discussion: some innovations needed for future competitiveness

Successful PV manufacturers in the future will be ones who can achieve the lowest cost in $/W which is $/module divided by Watts/module. So cost/module must be reduced and module efficiency must be increased. As mentioned earlier, most wafers for solar cells are grown by multicrystalline directional solidification, producing 600 kg ingots per growth run. This method has inherent solar cell efficiency limitations from both impurities and crystal defects. The cast silica crucibles employed are about 99.9% pure and introduce O, Fe, and other impurities into the ingot. A Si_3N_4 inside coating is applied to help mitigate these effects but is not entirely effective. Fe diffusion into the ingot makes large regions of the bottom, sides, and top of the ingot unusable and contributes to a lower minority charge carrier lifetime τ of the wafers. The multicrystalline structure is another τ limiter. While some grain boundaries such as twins are relatively benign, low

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Table 1
Silicon ribbon growth methods that were prominent in the "Silicon shortage" era.

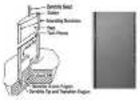
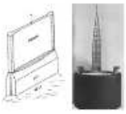
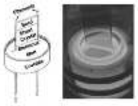
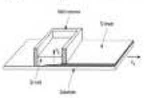
Method		Origination	Other Advantages	Problems
Si dendritic web growth (WEB)		1965 Westinghouse	Near single Thin (120 μ) Smooth surface Purity like CZ	Very slow throughput
Si edge-defined film-fed growth (EFG)		1972 Dow Corning	Polygonal tube growth possible with flat wafers laser-cut from the sides	Slow throughput High carbon Multi-crystalline
Si string ribbon growth/ESP (string ribbon)		1980 SERI/NREL	Relaxed thermal control	Slow throughput High carbon Multi-crystalline
Si ribbon growth on a substrate (RGS)		1994 AstroPower	Very high throughput	Multi-crystalline Small grain size Impurities Low efficiency

Table 2
Approximate throughput per machine and number of machines required for a 200 MW PV plant for various silicon crystal growth methods.

Growth method	Throughput (m^2/day)	No. of growers
Dendritic web	2	2,000
ESP/String ribbon	8	500
Capillary die growth EFG	20	200
Czochralski (CZ) growth	40	100
Directional solidification DS	70	57
Float-zone (FZ) growth	80	50
Electromagnetic casting EMC	600	7
Ribbon growth on substrate RGS	> 1000	< 4

Table 3
Abundance in the earth's crust and relative toxicity of the current major PV materials.

Element	Availability (% in the earth's crust)	Toxicity
Si	28.2	Salubrious
P	00.105	Toxic
Ga	00.0055	Low
Cu	00.0015	Moderate
As	00.00018	Toxic
Cd	00.000020	Toxic
In	00.000010	Low
Se	00.0000050	Toxic
Te	00.00000010	Toxic

angle grain boundaries can be very harmful to PV performance. The stresses related to the confined ingot in the crucible also generate dislocations within the grains and these are also harmful. So improved crucible purity as well as impurity barrier and stress mitigation coatings could be helpful in increasing the efficiency achieved with DS solar cells. Efforts to increase the crystal quality via bottom seeding the crucible with single-crystal seed plates cut from CZ crystals are also underway. This requires more precise thermal control, slower melt-in and cool-down times, and is more expensive to implement. Performance gains can be small due to small angle grain boundaries from seed plate misalignment, creep-in of multicrystalline structure from the crucible walls, and the Fe problem mentioned earlier. So the net gain is marginal unless the process is carried out very precisely.

Light-induced degradation due to boron–oxygen pairs in p-type silicon is a phenomenon that causes a slight initial drop in solar cell efficiency within days of light exposure after fabrication. Thus, there is a trend toward switching to n-based solar cell structures using phosphorous as the dopant rather than boron. A further benefit is that n-type material exhibits higher τ than that of p-type and can potentially achieve higher efficiencies for that reason. Because k_e=0.3 for P and 0.8 for B in silicon, it is easier to grow lengths of near-uniform-resistivity P-doped, n-type material by CZ growth than by DS growth. Accumulation of phosphorous at grain boundaries is eliminated in CZ growth and performing CZ growth in a semicontinuous fashion also leads to more uniform phosphorous doping. Semicontinuous CZ growth also has a number of other advantages for productivity and improved crystal properties [8,9]. It is likely that the fraction of PV silicon growth by the CZ technique will increase in the future relative to the fraction grown by multicrystalline DS. Other areas of improvement for CZ growth include continued reduction of power use, continued reduction of argon use, improved graphite hot zone life, higher-purity crucibles and/or crucible coatings, obtaining more pulls from a crucible, and improvements in semicontinuous crucible melt replenishment.

FZ growth, with its very high purity, relative freedom from oxygen and light-induced degradation with boron or other dopants, and high throughput (Table 2) is a good candidate for use in competitive future low-cost, high performance silicon PV modules. It has a major hurdle to overcome, however. The high-purity polysilicon feedstock must traditionally be in the form of long, straight, stress-free, crack-free, small-grained cylindrical rods which are likely to be more expensive to manufacture. There have been recent efforts to use granular silicon feedstock in the FZ process, and that may overcome the major hurdle.

Other innovative approaches being undertaken in crystalline silicon include direct casting of thin multicrystalline wafers, epitaxial growth of thin (40 μm), free-standing, 15 cm square single crystal wafers with > 15% solar cell efficiency on reusable substrates, and use of silicon as a substrate for III–V PV device structures. The free-standing epitaxial wafer process is particularly

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intriguing because it bypasses the polysilicon growth, ingot growth, ingot squaring, and wafering steps in Fig. 3 and goes directly from chlorosilanes to a single crystal wafer. The thickness can be at the minimum needed for light absorption, using a factor of 6 less silicon than is achievable with ingot growth and wafering. There is no dissolved oxygen (as is incorporated from the quartz crucible in CZ growth), and so light-induced degradation is minimal with either n- or p-type wafers.

The PV industry is beginning to recover from the “Excess capacity” problem, and some idle polysilicon capacity is expected to start coming back on stream in 2014. A major shakeout of upstream PV module suppliers has taken place and is still in progress. The number of such companies shrank from about 750 in 2010 to less than 150 in 2013. The most vulnerable are 2nd and 3rd tier crystalline silicon suppliers and smaller non-crystalline thin film module makers. There are mixed predictions on whether the learning curve will return to the historical mean, or whether PV module prices will stay lower than that. Most predictions are that they will stay lower. As discussed here, there are a number of avenues in crystal growth R&D to help achieve that.

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