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

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ABSTRACT

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, $CuIn_xGa_{1-x}Se_2$, 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.

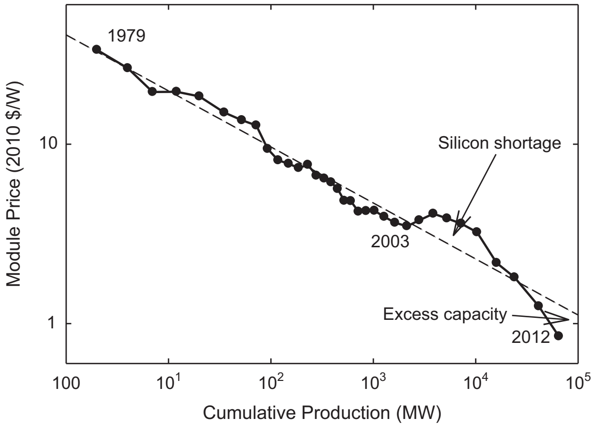

Fig. 1. The PV learning curve illustrating the change in price of PV modules (in 2010 $) as a function of cumulative module production (in MW).

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;

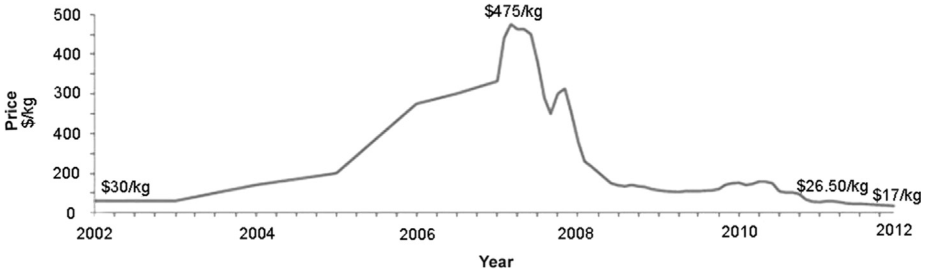

Fig. 2. The historical price of high-purity polycrystalline silicon.