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Silicon and wafer materials 2011 overview

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ABSTRACT

With more than 80% of PV module demand being satisfied by crystalline-based modules, the health of the silicon and wafer supply chain is of vital importance to the overall PV industry. This paper reviews the overall materials value chain from the manufacture of PV silicon to the wafer, prepared for manufacture of the cell. A glimpse is provided of the various market dynamics that exist in the supply chain, as well as the technology trends that influence or threaten the supply of wafers. Although the manufacturing routes are mature and well established, we also take a look at the possibility of novel and disruptive technologies altering the overall supply landscape.

Silicon supply

The PV industry today relies on various forms of silicon as a key raw material. More than 80% of installed modules use monolithic silicon wafers as the building block for the cell. Thin-film silicon modules may have reached a cost level that will allow them to compete on cost with the other leading TF module technology, CdTe. The supply chain for silane, the deposition precursor for TF silicon modules, is directly linked with that of polysilicon.

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There is an ever-increasing group of companies producing polysilicon. The production route starts with a common industrial raw material, metallurgicalgrade Si, which needs purification and refinement to become electronic-grade polysilicon. This refinement is carried out by gasification of the solid material, followed by gas phase distillation, and the subsequent transition back to the solid phase by chemical vapour deposition.

The two most common routes for conversion to the gas phase both start by reacting metallurgical-grade silicon with HCl to produce trichlorosilane (TCS). The next step is the purification of the TCS through distillation, after which it is used as the precursor for deposition in the Siemens process. An alternative is to catalytically decompose the TCS to monosilane (often called just silane) which is then used for the deposition precursor after purification.

The advantages of the TCS process lie in its simplicity and cost, whereas the extra step required for silane manufacture adds cost and complexity, but results in a higher quality product with fewer recycling concerns due to the absence of chlorinated molecules. The manufacture of TCS – or silane – and its subsequent conversion by CVD in the Siemens process is a large industrial enterprise which benefits from scale and a high standard of chemical engineering.

Polysilicon manufacturing plants are generally custom-built by specialist chemical plant constructors, and a high degree of expertise in running the process is required to successfully start and operate these large plants. Furthermore, the intermediates and byproducts of the gaseous route are both pyrophoric and toxic, driving the location of greenfield factories well away from areas of high population. The plants are also extremely power-hungry, requiring well in excess of 100kWh of power for the production of 1kg of polysilicon.

For world-class cost performance, polysilicon producers also need to recycle as much as of the feedstock as possible. A major byproduct of the TCS process is silicon tetrachloride, a toxic liquid which has few industrial uses, and which requires expensive disposal if it is not reconverted for use in the process. The efficient recycling of STC and other chlorosilanes is a key determinant of overall plant efficiency, although it adds operating cost and power consumption. While the polysilicon manufactured is not doped as n- or p-type at this point, the overall purity of the silicon is critical in determining its subsequent usefulness. High-purity silicon can be used in either IC or PV manufacture, whereas the PV market can accept lower-purity silicon. Lower-quality silicon can be compensated for to a great extent by process modification, but record-breaking efficiencies require high-quality starting materials. However, vertically integrated suppliers do have the ability to tune their cell production to make the best use of their captive silicon capacity, avoiding the variability of multiple suppliers, or opportunism of the spot market.

A further variation in the polysilicon supply side is the advent of granular silicon made by fluidized bed reactors. As discussed in the following, this may become more important as novel approaches to continuous Boule growth become more common.

Lastly, lessons are still being learned in regard to upgraded metallurgical grade (UMG) silicon, although demand remains at very low levels. UMG silicon is refined through metallurgical refining processes, which are cheaper than gaseous distillation. The capability to make cells with competitive efficiencies using UMG silicon has been demonstrated in practice, but the drive for cell efficiency retains the emphasis on PV grade-based cells.





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Regional trends

Historically, silicon manufacturing has followed the route taken by the chemicals industry, with major manufacturing centres in the U.S., Europe and Japan. With the development of the requirement for large quantities of silicon to fuel the explosive growth of the PV industry, some traditional suppliers of silicon have risen to the challenge by adding new capacity, but at the same time new players have started production, and others continue to emerge. These new players are shifting the regional concentration of silicon manufacturing capacity to Asia, and Chinese and Korean expansions are expected to add large amounts of capacity in the next few years.

Significant advantage can be gained in the correct selection of a manufacturing site. Electricity prices for polysilicon manufacturers vary by contract and local surplus. Some of the lowest-cost polysilicon is produced in regions with cheap hydroelectric power; in fact, a recent survey showed that global electricity prices were found to vary from US\$0.03/kWh to US\$0.10/kWh. This obviously represents a huge variation of cost, and is a driver of fundamental cost differentiation.

The explosive growth of polysilicon manufacturing capacity in China has been slowed somewhat by the lack of engineering capability to bring the plants to full yield quickly. Moreover, government regulations restrict the number of plants permitted, currently limited to less than 3000MT/yr, which accounts for a large part of the discrepancy between production and capacity figures shown in Figs. 1 and 2.

Apart from the obvious differentiation factor of silicon quality, production cost is a critical component in the ongoing viability of players in the silicon supply chain. Power is a key input into the manufacturing process, and large polysilicon plants need huge quantities of reliable, cheap power. Companies that can negotiate a bulk long-term supply of power at low market rates lock in price advantages. In times of tight supply all players can profit from higher prices, but in a cyclical industry where capacity addition is on a timescale significantly longer than that of demand fluctuations, overcapacity favours the manufacturers with the best scale and costs.

Global market forces

The silicon market is finishing one major long-term transition in its history, and will have to adapt to another over the short term. As little as three years ago, the consumption of silicon for ICs was equivalent in volume to that of the PV industry. Today, the picture is very different. PV silicon accounts for 76% of the silicon consumption in 2010, and will continue to increase in the future. This is a sea change in the drivers for supply, prioritizing volume, consistency, and cost over excellent quality. On the other side of the coin, the rush to add capacity, especially for newer players using a combination of custom and standard plant, has generated significant engineering challenges.

Crystallization and casting

In 2008 and 2009 multicrystalline cells maintained the majority of demand in 2010, with approximately 60% market share. However, we believe this will erode as cell and module manufacturers push to compete on efficiency.

The technology for both multicrystalline ingots and monocrystalline boules has not changed significantly. Nevertheless, efforts to increase yield and throughput are driving increased ingot sizes, as well as the development of semi-continuous monocrystalline boule growth by replenishing the crucible with granular silicon during pulling. Directional solidification furnaces have been increased in size from 450kg to 650 or even 900kg, with reduced cycle times to ensure improved productivity. Improved ingot and brick metrology have allowed better trimming to remove areas high in impurities.

The most important trend in the area of casting is the shift to mono wafers. The drive to efficiency has pushed cell makers to follow the path of selective emitters, wrapped contacts and back-contacted wafers to reduce shading and improve device efficiency. This in turn is driving a higher demand for mono wafers, and will result in increased demand for pullers over DSS furnaces.

Sawing

The conversion of boules and ingots to wafers is still accomplished by sawing, the technology behind which is undergoing rapid development to keep pace with the productivity requirements. Multiple wire slurry sawing (MWSS) has been used for wafering since the larger wafer became commonplace and rendered internal diameter saws impractical. The first significant recent change is a move from band saws for bricking and squaring to diamond wire saws. Not only does this reduce kerf, but the ability to make multiple simultaneous cuts reduces process time, while saws do not need slurry to make the operation more efficient.

In the case of IC wafers, where surface quality is critical to performance, the wafers can be thick enough to allow the removal of silicon by etch and polishing in order to achieve the required quality. In PV, the wet chemical etch of silicon to remove saw damaged material and to produce a low reflectance texture is kept to a minimum. Cells are also more tolerant to some surface defectivity. However, as the drive to thinner wafers to reduce cost is relentless, and efforts continue to produce



high-quality, low total thickness variation (TTV), production of wafers at 120 or 100 μ m continues. In contrast to IC wafers, the move to a larger wafer size is not yet seen as economically important. The added capital, difficulties in processing, and consequent reliability concerns are still high enough barriers to hinder the implementation of 210mm wafers.

SiC slurries are used in combination with steel wire and various carriers and additives. Wire thicknesses and SiC grit sizes are being driven down with the intention of reducing kerf and achieving thinner silicon wafers for efficiency improvements. The limitation of keeping tension on the wire without breakage remains a significant concern, particularly as wire diameter is lost during the cut and the sawn area increases.

Silicon carbide is an abrasive that is commonly used in industrial applications. However, the requirements of the wafering process means that a higher-grade green SiC is used due to its higher 'blockiness' which produces sharper grit at faster cutting speeds. This has to be balanced with wafer thickness variations across the wafer, leading to careful control of grit diameter and morphology. Additionally, smaller grit size is more expensive to buy, offsetting some of its advantages.

The high consumption of slurry for wafering has encouraged a strong response in terms of recycling. This industry accepts formulated slurries, and using centrifuge and separation technology, separates the silicon fines from the slurry components, and then separates the components into the individual carrier and abrasive. These are then supplied back to the user for combination into slurry for reuse when combined with virgin materials. The capital cost of these installations is significant, and scale requires that they be sited close to major wafering factories. As the industry develops centres of excellence, a concentration of wafering sites will develop, and thus an increasing amount of slurry can be recycled. The yields of this process are high, which keeps overall costs down, although there is a significant amount of capital tied up in the recycled slurry. This industry of slurry recycling has grown to approximately US\$660m in 2010, although plant suppliers are now offering onsite recycling systems that allow large wafering companies to recycle slurry in-house. Despite this uptake in recycling, the supply of sawing abrasive was found to be tight for much of 2010.

Despite the efficiency of the value chain, the drivers to switch to diamond wire for wafering are compelling. Although currently very few manufacturers use this method to cut wafers, diamond wire supports higher cutting rates, reduces sawing time and increases productivity, while only requiring water as a cooling medium.



Efforts are underway to develop silicon recovery methods for both the MWSS and diamond wire approaches. Potentially the largest available gain in the silicon wafer value chain, recovery methods could see the re-use of approximately €0.1 to €0.12/W of wasted silicon. Although this remains a challenging feat, it will be easier to perform from water than from a PEG/SiC mixture, and processing costs cannot exceed the value of the materials recovered. Another option is the sale of the high purity mixture of SiC and silicon for processing in the ceramics industry.

The uptake of slurry recycling can also impact other potential materials suppliers indirectly; for example, slurry performance can be improved by the addition of additives to both suppress agglomeration and help the cutting process. Current recycling technologies cannot easily remove these additives, nor can their concentration be well controlled. Consequently, recycled slurries are normally left additive-free in order to avoid these problems, a feature that has made market entry difficult for suppliers of these additives.

Novel technologies

The demonstrated limits of sawing lie at around 80µm today, but research and development continues to strive towards achieving silicon thicknesses of the order of a few tens of microns. The preferred routes today include implantation and stress cleaving, epitaxial layers on carrier substrates, silicon on porous silicon and laser cutting. Once the thin silicon slices are produced, the challenge remains of developing effective processes and equipment to process ultrathin wafers. However, the combined challenges of developing the wafer-slicing methodology and the subsequent process technology mean that implementation of these technologies are several years in the future.

Conclusions

The entire PV industry is still reliant on the political goodwill of the regional governments that support the commercial and residential investors in PV. Supply chain participants have to manage the vagaries of political decision-making while also developing strategic and tactical plans to gain share in a rapidly expanding market.

While some materials involved in the supply of wafers are highly transportable (silicon, slurries, crucibles, etc.), services such as recycling are highly localized, and cannot economically be centralized. Factors such as labour, power and cellmaking clusters have dictated that the silicon, casting and sawing supply chain is globally distributed, and will remain so.

With the demand for PV-grade silicon in 2010 well over 100,000MT, and silicon cost still at about 60% of the module bill of materials, hopes for price declines through scale and increased competition become vital if we are to facilitate the final project returns. The background of reduced subsidies in nearly all PV markets will contribute further to the squeezing of profit pools, and each step will become commoditized.

On the other hand, the sheer scale of current demand – and the potential for an increase of perhaps an order of magnitude over the next decade if forecasts are realized – means that this is a market for companies with either deep pockets or strong market credibility that will allow them to raise the large amounts of capital needed to service a utility-scale PV industry that is capable of supplying 100GW of annual capacity or more.

About the Author

Mark Thirsk is Managing Partner of Linx Consulting. Mark has over 20 years' experience spanning many materials and processes in wafer fabrication. He has served on the SEMI Chemicals and Gases Manufacturers Group (CGMG) since 1999, acting as Chairman between 2001 and 2003.

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