Opportunities for advanced chemicals and materials in solar cells and modules

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ABSTRACT

The rapid growth of the solar energy industry owes its success to the development and production of mono- and multi-crystalline solar cells. This growth has been limited in recent years due to the lack of available supply of polysilicon, the key raw material for making the wafers that serve as the basis of the solar cell. As a result of this limitation, the price of polysilicon has increased dramatically and this has led to significant new and planned capacity expansions. These new capacity expansion announcements have been highly publicised, with little additional outside focus on other chemicals and materials.

This paper will examine technical and business aspects of the materials business as it relates to the flat plate solar industry, including the current situation on materials for crystalline silicon cells as well as other key chemicals and materials used in the production of various thin-film solar cells. In addition, we will discuss the types of chemicals and materials consumed and the business opportunities for electronic chemicals and materials suppliers.

Introduction

The foundation of the solar industry is based upon the phenomenon of the photoelectric effect. Many different semiconducting materials can be utilized to obtain this effect, and optimization of the efficiencies and better matching of band gaps through process and materials choice are being pursued every day. Early photovoltaic products relied on higher efficiency compound semiconductors, and were primarily for military and aerospace applications, where higher costs were acceptable. The majority of today's commercial cells are silicon-based, and cost reduction efforts, as well as economies of scale, promise to bring PV power generation into competition with grid power. However, silicon remains an expensive commodity, and focused attempts to develop next-generation solar cells include such thin-film technologies as tandem cell silicon or replacement semiconductor materials such as CdTe (cadmium telluride), or CIS/CIGS (copper indium selenide/copper indium gallium selenide) materials. These thin-film products are all typically built on a glass, steel or plastic substrate. This paper's primary focus will be a review of the chemical and material requirements for silicon and thin-film solar cells and modules.

Crystalline silicon solar cell manufacturing

Crystalline cells still account for over 90% of solar cell production. The production of crystalline solar cells has parallels to the production of silicon semiconductor devices such as bipolar and analog ICs. Both start with a silicon substrate which is then doped to produce a diode upon which electrical contacts are provided, similar to the interconnect structure in a chip. Integrated cell producers will typically source PV-grade polysilicon, which is then either grown into single crystal boules or polycrystalline ingots. The boules or ingots are cut into wafers which pass onto the cell manufacturing process. Producers trade off the lower cost of polysilicon wafers with their lower conversion efficiency.

Until recently, the dominant demand for high-purity silicon came from IC manufacturing, but industry dynamics resulted in a significant overcapacity in manufacturing, resulting in price competition and excess supply. This low pricing made reinvestment in capacity unattractive but helped early growth in the solar cell industry. Skyrocketing demand for crystalline silicon PV modules has reversed this situation, driving demand for huge increases in polysilicon capacity.

However, the scale of reinvestment over the last few years is massive, with existing leaders such as Hemlock Semiconductor, Wacker, REC, Tokuyama, and MEMC investing to maintain share, as well as new companies such as LDK and DC Chemical entering the market. Overall, we feel the impact of this capacity build will lead to a large polysilicon oversupply situation starting in 2009 or 2010, as illustrated Figure 1 (silicon capacity has been converted to megawatt equivalent).

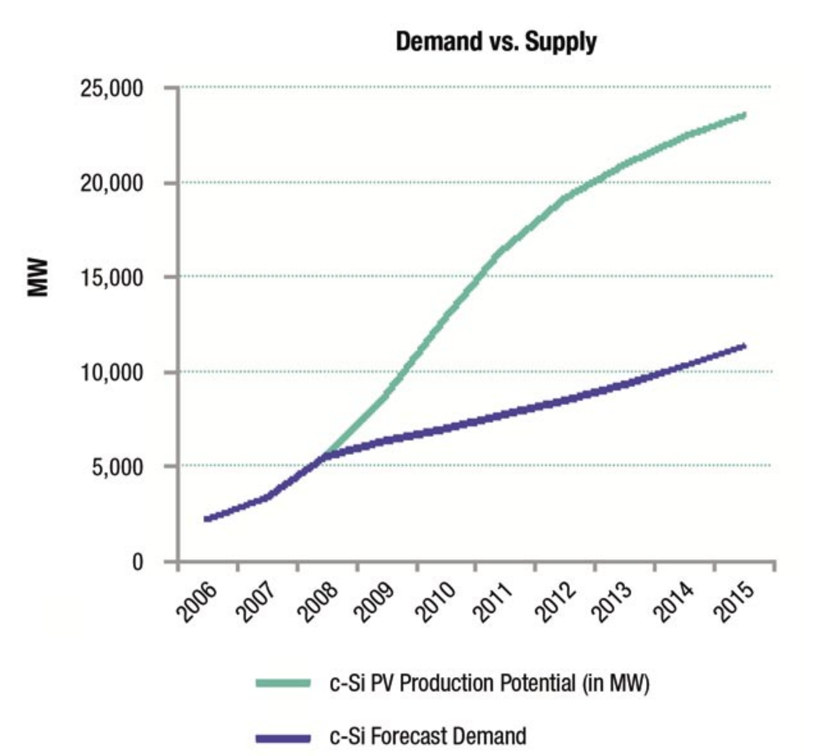

Figure 1. Polysilicon supply and demand balance for Si solar cells.

Other key steps and materials used to produce crystalline silicon cells include the following:

Wafer sawing. A major cost factor in all large wafer manufacturing (except ribbon growth) is the kerf loss in sawing the wafers. Even as wafer thicknesses are reduced, kerf loss remains between 40% and 50% of the starting silicon weight. Sawing consumables of silicon carbide abrasive and polyethylene glycols are largely recycled.

Wafer texturizing. To increase cell efficiency, the wafer surface is roughened by one of several processes, which are dependent on the crystal type of the wafer being texturized. Polycrystalline wafers use HF and HNO_3 etches for texturization, sometimes followed by NaOH rinses. Solutions are generally electronic-grade acid mixes of 25% to 40% concentration. Monocrystalline wafers use NaOH and KOH etches, which take advantage of the crystallographic anisotropic etch rates in silicon, and leave a pyramidal structure on the surface.

Junction diffusion and doping. The most common process for doping is gaseous diffusion of electronic grade $POCl_3$ delivered in a tube or belt furnace at about 900-950°C with nitrogen carrier gas. $POCl_3$ is commonly delivered in quartz bubblers in volumes of 1000ml to 1500ml, and are connected to the furnace gas feed. In advanced processes, selective doping technology is used to form emitter and base regions, and to improve contact resistances to improve cell efficiency. Currently, most monolithic cells are manufactured without selective doping, but tests have shown improvements of 0.2% to 0.4% of absolute efficiency through the use of selective emitters. Screen-printed materials are being employed, but tests with ink-jetted materials are under development. Printed dopants are usually dried in infrared belt ovens, followed by an 850-950°C firing for 3-5 minutes in a tube furnace or belt oven.

Anti-reflective coating (ARC) deposition. To capture as much incident radiation as possible in the final cell, an anti-reflection layer is added to the front side of the cells over the texturized surface. In the vast majority of cell lines, this is a PECVD-deposited Si_3N_4 layer of a thickness chosen to incouple the incident light.

Metal grid deposition. Screen-printed Ag and Ag/Al pastes are used for contacting silicon solar cells passivated with Si_3N_4 coatings. Inks are deposited with high-speed screen-printing systems through emulsion screens. Inks are formulated with glass frits that aid reaction with the nitride and oxide on the surface of the silicon. During the firing process, the glasses and additives contained in the inks react with silicon nitride to form a low-resistance contact while providing good adhesion to the wafer and good solderability.

Back-surface field metallization. Back surface field (BSF) metal is coated across the back of the cell. BSF metallization films are normally printed with pure aluminum inks and can be formulated to be compatible with the back-side grid ink, and, although dried separately, can be co-fired.

Moduling. To seal the silicon cells from the environment, a combination of glass and polymer films are laminated around the cells. Key moduling components are based on advanced polymers and include an EVA encapsulant material and a protective backsheet. The backsheet is usually laminated to combine film properties to control UV damage and moisture ingress, dependent on ultimate application. Critical materials in the laminate include PVF Films, PVDF films and PET films.

However, due to the inherent expense of polysilicon, limits to wafer thickness, cell efficiencies, kerf loss and other factors, many companies are aggressively pursuing thin-film solar cells.

Thin-film solar cells

Thin-film cells offer a route to low-cost power by reducing the amount of high-cost materials, and by automating manufacture. Strategies include developing cells from thin films of silicon or other semiconducting materials such as CdTe, or CIS/CIGS.

The 'hottest' silicon thin-film manufacturing technology combines the overlapping band gaps of amorphous and microcrystalline silicon deposited by CVD. Equipment manufacturers are drawing on technology similar to that used in thin-film display manufacture.

In fact, the production of tandem cell thin-film solar cells is more similar to the production of TFT LCD in that the starting substrate may be a sheet of glass (equivalent to generation 8 TFT LCD glass in the case of Applied Materials' production tools) or a steel of flexible substrate. Materials supply for these manufacturing lines consist primarily of specialty gases and PVD targets sandwiched between float glass. Projected economies of scale have prompted several companies to plan 1GW-size manufacturing lines, requiring significant supply infrastructure.

Tandem cell or micromorph technology is being promoted by complete turnkey manufacturing lines offered by suppliers such as Applied Materials, Oerlikon and Ulvac. This technology is reliant upon PECVD for the absorber layers, and as a result, there is a large specialty and process gas requirement, including silane, ammonia and chamber cleaning gases such as NF_3 or F_2. The Oerlikon process also uses PECVD for the back contact layer, whereas Applied uses PVD deposition. The cell is enclosed with another layer of glass that has a polymeric coating of PVB (polyvinylbutyral) for adhesion and moisture protection.

Non-silicon thin films

Other thin-film solar technologies, including CdTe and CIS/CIGS, have had to overcome multiple obstacles to develop commercial sales. Firstly, cell developers have had to develop the technology, but additionally, manufacturers suffer from the lack of standardized manufacturing equipment. To date, CdTe manufacturers, such as First Solar, have been the most successful in developing viable manufacturing infrastructure. The variation of absorber deposition options for CIS/CIGS has remained a significant obstacle for these technologies.

Thin-film materials are typically deposited on a glass substrate. Some cell producers are also investigating steel and flexible polymeric-based substrates. Key materials used in these applications fall into the category of specialty metals and include the following: Mo, Cu, In, Ga, Se, CdTe, and CdS. As there is little commercial background in widespread mass-production processes involving some of these films, a variety of processes are used to deposit the complex thin-film materials for these cells including sputtering, chemical bath deposition, sublimation, vapor-transport deposition, electrochemical deposition and chemical vapor deposition. In addition, transparent conductive oxides will be used and some processes will utilize SnO, ZnO and possibly ITO.

Opportunities for electronic chemicals and materials suppliers

The major areas of chemicals and materials opportunities can be found in the following segments:

- Polysilicon and upgraded metallurgical grade silicon (UMG)
- Bulk and specialty gases
- Acids and inorganics
- Deposition precursors
- Metal pastes
- Polymeric films for encapsulation, packaging and protection
- Specialty metals for CIS/CIGS

As the industry continues to grow, most of the leading chemicals and materials suppliers will continue to jostle for position or enter the space because they cannot afford to be locked out of an emerging global market, as it would impact perceptions in the financial markets. At the same time, the solar industry is benefiting from a massive influx of talent from other thin-film processing industries including semiconductors – especially in the U.S. and Europe – and TFT LCD. Examples of companies that have crossed the line from one segment to another include Cypress (SunPower), Sharp, and Qimonda. Factory sizes are being increased from tens of MW, labor-intensive operations to GW-scale plants with high degrees of automation and very sophisticated chemicals, materials and logistics capabilities.

The solar industry has material multiple challenges, including:

Raw material availability. From polysilicon for crystalline cells, and pastes

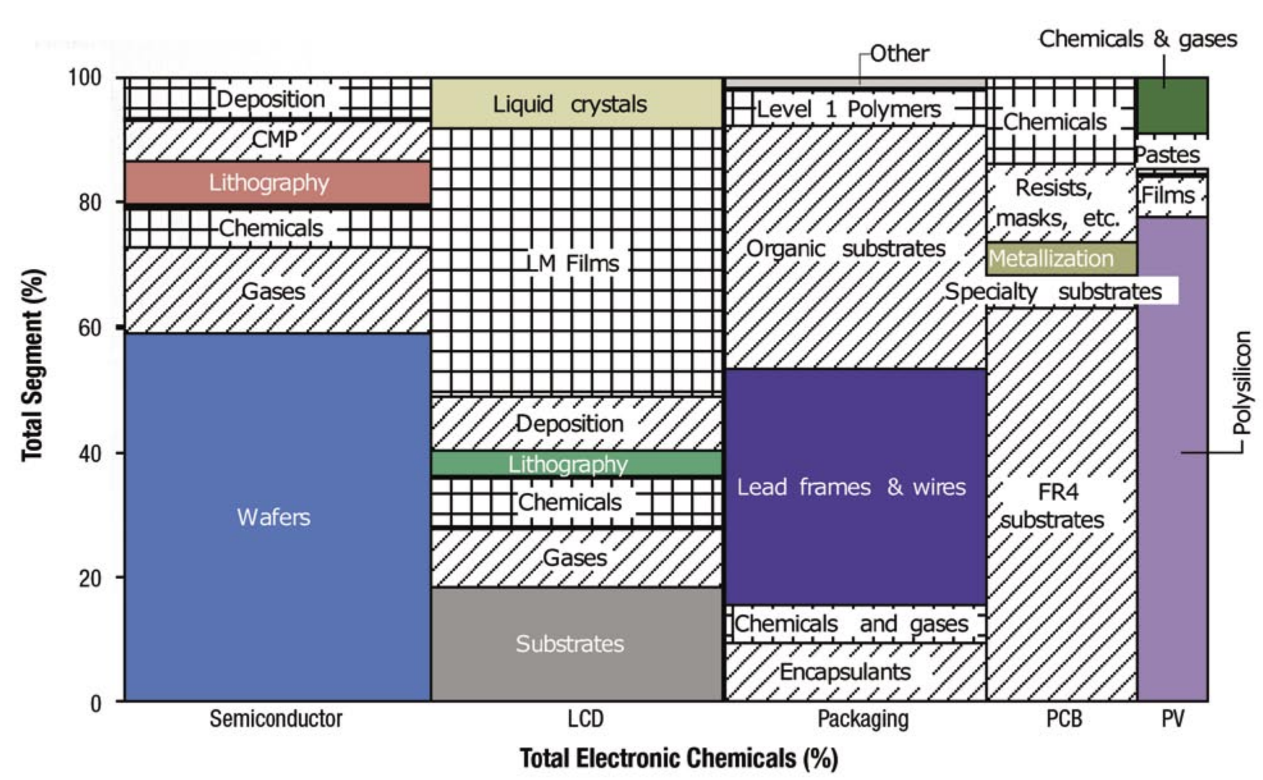

Figure 2. Electronic Chemicals and Materials Landscape in 2007. The electronic chemicals and materials market is estimated at US$72 billion in 2007.

for gridding to the limited global supply of In and Te, ensuring viable supply chains at competitive costs is key. This concern currently seems more severe for In than Te because of competing uses. The primary challenge will be to reduce absorber thicknesses (film or wafer), while maintaining state-of-the-art performance.

Need for high-throughput, low-cost processes. All successful wafer and thin-film companies have devoted resources and effort to developing production processes and tools to enable their technology. This appears to be inefficient, and will inhibit propagation of advanced manufacturing technologies. AMAT and Oerlikon will likely enable high-volume processes in tandem thin-film technologies, but adopting learning from other industries such as IC manufacturing will enable key cost reduction. Fortunately, the chemicals and materials suppliers in the electronics industry have been exposed to these types of challenges in the past in the semiconductor industry and TFT LCD industry. The materials requirements for solar cells and modules are rapidly emerging and represent another segment of the electronic chemicals and materials market as shown in Figure 2.

Most of the chemicals and materials that come in direct contact with the cell are 'electronic grade,' with consequent purity requirements and demonstrated supplier reliability. Many of the leading suppliers to the solar cell and modules industry have a long history of serving the electronics industry; however, new entrants do not have this experience and this new industry represents a novel challenge for them.

> As manufacturing scale increases, the volume demands of the PV industry will become significant, and those suppliers that can meet expectations can expect to participate in a strong growth industry.

While there are limited opportunities for novel materials in today's solar industry, the dual requirements of low-cost manufacture, coupled with the need for electronic-grade purity and supply chain reliability, will be a balancing act that could challenge suppliers. As manufacturing scale increases, the volume demands of the PV industry will become significant, and those suppliers that can meet expectations can expect to participate in a strong growth industry. Critical success factors in the solar industry include applying synergies (shared infrastructure, materials technologies, etc.) and learning other electronic segments (semiconductors, TFT LCDs, advanced packaging, etc.).

Lastly, of course, the development in cell technology continues. Materials innovation, process innovation, and applying creativity in materials use, recycling and choice are likely to be vital in aiding novel cell technologies to market, and in offering opportunities to suppliers engaged in these segments.

Reference

The insights and perspectives for this article were derived from Linx Consulting's annual report on chemicals and materials in the solar industry – *Advanced Chemicals and Materials for Photovoltaic Cells and Modules.*

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