The rapid expansion of photovoltaic manufacturing capacity has brought significant developments in technological capabilities, most notably the development of thin film photovoltaics (PV). Historically, PV cells are made using silicon wafers (known as crystalline silicon technology), but in thin film technology, the cells are formed by growing the active layers on lower cost substrates. This has opened up the prospect of increasing the manufacturing scale thanks to more simplified process steps.

While the mass production of thin film silicon PV modules may still be in its infancy, progress has been rapid. In 2008 early manufacturing adopters were achieving around $1.50 cost per watt, while $0.70 is predicted for 2011. Over the same period, manufacturing throughput is predicted to double, while materials costs will fall by around 50 percent. All these factors are critical in the drive towards grid parity and widespread adoption of thin film PV.

Although fewer than 25 different gases and chemicals are used in solar cell manufacturing, compared with more than double that amount for semiconductors, the volumes required are significantly greater and supply chain management presents unique challenges.

**Film Deposition**

Electronic device manufacturing processes such as those used in thin film photovoltaics are highly complex and multi-stage. The critical process step in all thin film silicon technologies is deposition of doped silicon film from a silane precursor in a Plasma Enhanced Chemical Vapour Deposition (PECVD) system. The result is a thin film of silicon on glass. Typically, hydrogen is also introduced to control the kinetics of the film growth. Dopants are incorporated through precursors such as trimethyl boron (TMB), diborane (B\(_2\)H\(_6\)), phosphine (PH\(_3\)) and methane (CH\(_4\)).

**TCO Coating and PVD Glass Coating**

Another important step in some thin film PV cell manufacturing processes is the deposition of a transparent conductive oxide (TCO) film on the front glass. This is typically tin oxide or zinc oxide deposited via sputtering or using an organometallic precursor such as diethyl zinc (DEZ). The application of a back contact metal layer by physical vapor deposition occurs during the PVD glass coating process. This typically uses argon for aluminum sputtering.

**Chamber Cleaning**

Between deposition steps, the equipment chambers require cleaning, and this is typically carried out with a reactive gas containing fluorine atoms. The film deposition process also results in silicon deposition on other surfaces in the PECVD process chamber such as the showerhead and chamber walls, which must be periodically cleaned.
Inside a Thin Film Crystalline Solar Cell Fabrication Plant

Typically, a fluorine-based etch process using nitrogen trifluoride (NF$_3$), sulphur hexafluoride (SF$_6$) or pure fluorine (F$_2$) is employed for this purpose.

Linde’s (www.linde-gas.com/electronics) recommended solution for chamber cleaning on cost, efficiency, and environmental grounds is on-site generated fluorine. (See “Linde’s On-site Fluorine Helps Reduce Environmental Impact, p. 3.) Compared to nitrogen trifluoride, the default chamber cleaning gas, pure fluorine is a much more effective cleaning agent—it can be broken down into more reactive compounds more quickly and with less energy than NF$_3$. This reduces the cleaning time by more than 60 percent and uses up to 60 per cent less power in the process with zero global warming potential.

Unique to fluorine is the way it is supplied—the gas is manufactured on the customer’s site on demand by a compact, modular plant. Linde is the only gas company with this capability, and over the last ten years more than 30 of these systems have been installed on customers’ sites in the TFT-LCD, semiconductor, and PV industries.

Dopant Gas Blending

As the scale of PV manufacturing increases, very high volumes of dilute dopant gases are required. Linde has developed a proprietary blending system which produces the dopant gas mixtures on-site. Customers benefit from improved security of supply and reduced transportation and changeout costs, helping to meet both carbon-footprint and cost-reduction roadmap targets.

**Bulk Silane Storage**

Silane is one of the most critical gases used for thin film cell fabrication. Due to the large volume requirements—typically 500 kg per MW per year—silane is generally supplied in either multi-cylinder bundles or ISO modules containing up to 6,000 kg. Given silane’s potentially hazardous properties, storage and delivery systems require careful design, installation, and operation with all aspects of the bulk silane supply chain.

**On-site Gas Generation**

Thin film silicon solar cell manufacturers require large volumes and a constant and reliable supply of nitrogen, oxygen, hydrogen, and compressed air. On-site supply systems are typically built around standardized components to ensure maximum cost-efficiency and can be designed for year-round uninterrupted supply (8,760 hours) through incorporation of redundancy. Systems can be automatically controlled and are monitored by the nearest gas facility to ensure a reliable gas supply.

**Bulk Compressed and Liquefied Gases**

A secure and reliable supply of essential bulk gases, such as nitrogen, oxygen, argon, hydrogen, and helium, are demanded by thin film silicon and crystalline silicon customers alike. These products are typically manufactured by global networks of high purity gas plants and delivered by road in liquid or compressed form to storage facilities on the customer site. Gas suppliers like Linde Gas typically offer a comprehensive design and installation service for bulk gas supply including storage tanks, evaporators, purifiers, filtration, and corresponding ultra high purity distribution systems. This ensures a safe and efficient operation with continuous product availability.

**Cylinder Gases and Dopants**

Electronic specialty gases, including silane, nitrogen trifluoride, ammonia, and dopant mixtures, are typically shipped in a variety of container sizes depending on application, ranging from individual cylinders to ISO containers. Gas suppliers like Linde Gas can offer a full range of special gases to support photovoltaic manufacture.

**New Challenges**

Gas suppliers are evolving from being “traditional suppliers” to becoming integral parts of the manufacturing industry as PV manufacturers seek strong, reliable, and knowledgeable partners with expertise in the wide range of special materials used in the thin film silicon production process. As the industry grows, other challenges for manufacturers include managing safety and environmental issues, and developing materials technology that will both reduce costs and increase cell efficiency.


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