

Gas Usage and Cost Management in Photovoltaics and High-Brightness LEDs

BY DR. ANISH TOLIA

A view of the gases critical to PV and HB-LED manufacturing, and how they determine the cost-effectiveness of these devices.

Energy is one of the mega-trends driving the world economy today. Clean energy, particularly photovoltaics (PV), is an area of major investment and growth as a source of green energy production. Industrial gases play a very significant role in the manufacturing of photovoltaic cells and a critical part in reducing cost of PV in the march to grid parity.

Lighting applications account for around one third of global electricity usage, so energy efficient lighting can significantly reduce growth in electricity demand. High-brightness LED (HB-LED) lighting is seen as the ultimate low-power, long-life lighting technology. The HB-LED industry is also growing rapidly at over 30% per year. Once again, industrial gases play a significant part in the technology used to manufacture LED chips.

This article aims to highlight the role of gases in these two important green technologies with emphasis on efficiency, cost management and scaling for large scale manufacturing.

Photovoltaics

By the end of 2010, approximately 40GW of solar modules were installed worldwide. 16.6GW of modules were added - this is solar module installations rather than manufacturing capacity. While the EU demand accounted for

| Technology | Relative gas intensity |
|---------------------------|---------------------------------------|
| Crystalline silicon cells | 1.0 (excluding polysilicon and wafer) |
| CIGS / CdTe thin film | 0.9 – 1.2 |
| Silicon thin film | 10-20 depending on equipment supplier |

Table 1. Relative gas intensity vs. PV technology

80% of the PV capacity, manufacturing is shifting to Asia. For instance, China produces around half of the world's crystalline silicon cells and modules.

The market for gases used in PV manufacturing is large, but varies significantly depending on which technology is employed to manufacture the PV cells (see Table 1).

Gas requirements for copper indium gallium diselenide (CIGS) and cadmium telluride (CdTe) technologies are largely bulk atmospheric gases such as nitrogen or argon, while crystalline or thin film silicon requires a much wider range of atmospheric and special gases.

Gases in Crystalline Silicon Solar Cell Manufacturing

While manufacturing processes will vary between different equipment platforms, the gas component of a crystalline silicon (c-Si) cell is typically between 2 and 3%. However, with around 60% of the overall cell costs contributed by the silicon wafer itself, cost management has largely focused on optimizing wafer production and reducing silicon losses in the ingot sawing process. Table 2 lists the typical gases used in c-Si processes.

In the primary gas using process, silane and ammonia are used in combination via plasma deposition to grow a silicon nitride anti-reflective coating, while carbon tetrafluoromethane is used to plasma etch certain parts of the wafer.

Currently, many other process steps such as etching and cleaning are carried out using wet chemicals. However, as cost reduction drives wafers to ever smaller thicknesses (sub - 120µm) some wet processes will become challenging—not only because of the physical impact on the wafers, but also due to the very large scale of chemical

| Product | Typical Grade | Typical Package (<500 MW) | Typical Package (>500 MW) |
|---------------------------------------|---------------|-------------------------------|----------------------------|
| Silane (SiH ₄) | Electronic | Cylinder/Cylinder bundle | ISO module (6000kg) |
| Ammonia (NH ₃) | Electronic | Tonne tank/Drum | Drum/ISO module (20000kg) |
| Tetrafluoromethane (CF ₄) | Electronic | Cylinder / Cylinder bundle | Cylinder bundle |
| Nitrous Oxide (N ₂ O) | Electronic | Tonne tank | Tonne tank/Cylinder bundle |
| Nitrogen (N ₂) | Electronic | Liquid tank | On-site generator |
| Oxygen (O ₂) | Electronic | Cylinder bundle / Liquid tank | Liquid tank |
| Argon (Ar) | Electronic | Liquid tank | Liquid tank |
| Hydrogen (H ₂) | Electronic | Cylinder bundle | Liquid tank |

Table 2. Typical gases used in c-Si processes (tonne = metric ton = 2204 lbs)

supply required to serve ultra-high throughput manufacturing. Thus new gas applications may emerge for dry etching, requiring the use of fluorine based gases.

Gases Used in Thin-Film Silicon Manufacturing

Thin film silicon solar cells use amorphous silicon on a substrate, usually glass. They offer a significant advantage in manufacturing large size panels—up to 5.7 square meters, depending on the technology. A further significant advantage that this technology enjoys is the availability of large scale turnkey production equipment developed and proven in the

flat panel display industry.

After showing initial promise, thin film silicon underwent a turbulent time due both to economic and technical factors. Recently however, that technology is seeing a new wave of activity, particularly in Asia, where new equipment manufacturers have entered the market. In some cases these new equipment sets require radically different gas supplies than the first generation thin film production lines. In all cases though, gases are a much more significant portion of the bill of materials, representing up to 15% of direct costs. Figure 1 shows the mix of gases required for 3 different equipment platforms.

With gases playing such an impor-

tant role, adopting the optimum supply mode for these critical materials is essential not only to ensure a clear scale-up path, but to ensure that cost reduction opportunities are fully exploited.

On Site Generation of Bulk Gases

As thin film silicon fabs grow in scale, the economics favor on-site generation of major bulk gases such as hydrogen and nitrogen (see Figure 2). This eliminates the liquefaction/compression and delivery cost and enhances security of supply.

On-site hydrogen generation can be achieved through the installation of steam methane reformers or electrolytic cells. On-site hydrogen is the preferred delivery method for flows exceeding 150 Nm³/hour, flows that are hard to serve with a traditional compressed trailer supply. Nitrogen can also be generated on-site via packaged N₂-generators. A minimum consumption of 1500 Nm³/hour makes this a cost effective solution.

Optimizing Chamber Cleaning

Depending on the OEM platform, more than 50% of the capital cost and over 40% of the direct materials cost are related to the CVD process that deposits the active silicon layers. These CVD chambers require frequent cleaning of silicon residue. Replacing current methods (NF₃ or SF₆) by fluo-

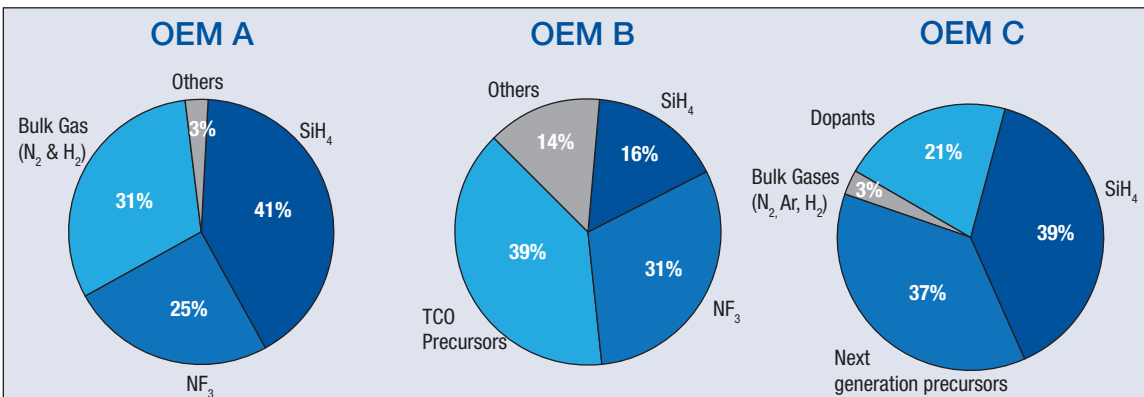


Figure 1. Mix of gases required for 3 different equipment platforms.



Figure 2. As thin film silicon fabs grow in scale, the economics favor on-site generation of major bulk gases such as hydrogen and nitrogen.



Fig 3. On-site generation of fluorine

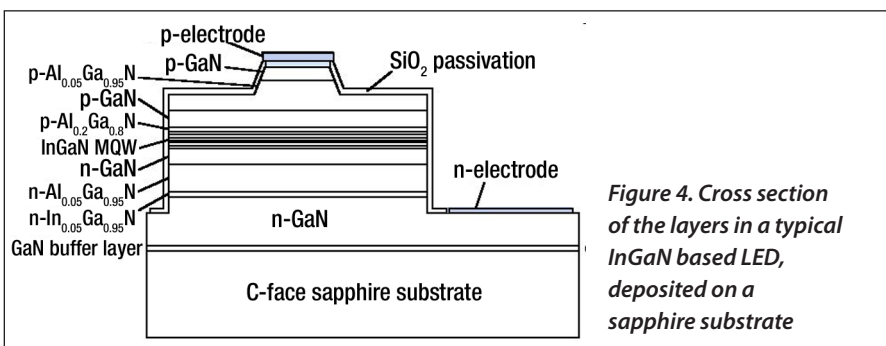


Figure 4. Cross section of the layers in a typical InGaN based LED, deposited on a sapphire substrate

rine (F_2) can cut cleaning costs by up to 40% and cut cleaning time, leading to an increase in throughput. Fluorine can be generated on-site using packaged fluorine generators such as those shown in Fig. 3.

Silane

Across all OEM platforms silane is used in large quantities. While silane unit cost reduction opportunities exist due to the large demand, by far the largest reduction in costs is achieved through process improvements to reduce the silicon film thickness. Indeed, over the past few years the quantity of silane used per MW has more than halved as OEMs focus on this area.

Doping Materials

Doping materials such as phosphine and tri-methyl boron are traditionally supplied as low level mixtures in hydrogen. For a large scale thin film silicon fab, many hundreds of such cylinders would need to be shipped each year. Since hydrogen is generally available as part of the overall gas supply solution, costs and logistics can be significantly reduced by shipping pure dopants and making the blends on-site with a packaged, precision blending system.

LED Solid-State Lighting

The market for “white” light emitting diodes, also referred to as High-brightness LEDs (HB-LED), has grown tremendously in the last two years. The main drivers of this growth have been the application in flat panel display back-lighting, where low temperature, power-efficient and compact light-sources are required, and also the nascent adoption of LEDs in place of fluorescent or incandescent lighting, for power efficiency.

The most critical process in LED manufacturing—and the most materials cost-intensive one—is the growth by epitaxial deposition of the active semiconducting layers. This is accomplished by metal organic chemical vapor deposition (MOCVD), creating metal nitride compounds from volatile organometallic precursors such as trimethyl gallium. Figure 4 shows the cross section of the layers in a typical InGaN based LED, deposited on a sapphire substrate.

All of the critical device layers are deposited

on the substrate from the gas phase inside a high temperature MOCVD reactor. The typical range of gases used is as follows:

- Atomic nitrogen source: ammonia (NH₃)
- Dopants: gaseous molecules containing boron and phosphine
- Etch gases: nitrogen trifluoride (NF₃); sulphur hexafluoride (SF₆); carbon tetrafluoride (CF₄)
- Process diluant: hydrogen (H₂)
- Pumping and vent gas: nitrogen (N₂)
- Other recipe ingredients: silane (SiH₄), nitrous oxide (N₂O), methane (CH₄), helium (He)

can poison the LED device, significantly reducing its light output.

Each MOCVD process chamber consumes approximately ten tonnes per annum of ultra-pure ammonia gas, which is kept in excess in the chamber atmosphere during deposition, while hydrogen is consumed at approximately half this rate. The MOCVD deposition process is slow, each batch takes several hours, hence sustained flows of ultra-high purity gas are required. With the new generation of LED fabs planned to include 50 to 100 or more MOCVD reactors, a cost-effective high volume /high purity delivery of gases must be achieved in order to support these fabs. Table 3

lenging properties of ammonia which must be managed.

Moisture control: While specifications typically require moisture levels of 50 parts per billion or lower, ammonia's hygroscopic nature means that keeping the gas dry through filling of shipping containers, delivery to the customer and connection to piping for distribution to the process tools, is a significant challenge. Overcoming this requires careful design, installation and quality control. Generally, the highest semiconductor industry cleanliness standards are applied including the use of electro-polished stainless steel, high-purity leak-tight valves etc. to minimize risk of moisture contamination and to speed up system dry-down. All of these measures also drive up cost.

Vaporization

Ammonia is a low vapor pressure gas, with a high latent heat of vaporization. Shipped as a liquid, a significant amount of energy is required to deliver a suitable pressure (typically >100 psig) and flowrate (100's to >5000 slm) of vapor to the process. Since moisture tends to concentrate in the liquid phase, high vaporization rates can also drive higher moisture contamination into the gas phase in aerosol droplets. To avoid carryover of moisture to the process, a significant amount of liquid NH₃ (typically at least 10%) is left in the container to be returned and reprocessed or disposed of, further increasing cost.

The combination of these interacting problems creates practical limits on supply via conventional gas packages. Using container heating, supply rates today are limited to around 1500 slpm per system, hence new supply modes must be deployed in order to meet the demands of new fabs in a cost efficient manner.

Managing Hydrogen

As with photovoltaics, delivering high purity hydrogen (99.999%) cost-effectively to large fabs is impacted primarily by the regional variations in the source and specification of the hydrogen supply. In Europe, liquid hydrogen is commonly available and provides an economic supply mode for many high flow demands. In China, compressed hydrogen by tube trailers is available but costs are driven by the distance to the

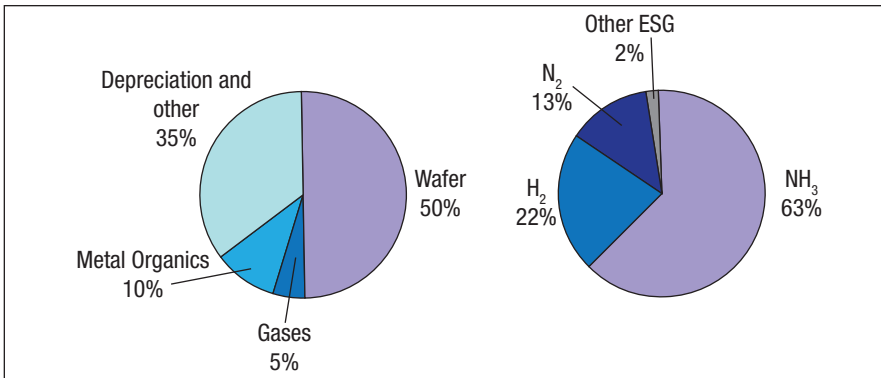


Figure 5. Approximate break down of the cost structure of LED chip manufacturing, not including the device packaging (ESG = electronic specialty gases)

An approximate break down of the cost structure of LED chip manufacturing (not including the device packaging) is shown in Figure 5

Ammonia (NH₃) and hydrogen (H₂) represent the largest portions of gas costs and are also critical to the performance of the LED device, since moisture and oxygen contamination in trace quantities

shows gas delivery schemes that can meet both flow and purity specifications that are available to customers today, and their applicability to LED fab scale.

Managing Ammonia

In order to provide the quality and quantity of gas to enable cost-effective high-volume LED fabrication, there are two chal-

| MOCVDs | <25 | 25 | 50 | 100 | 200 |
|----------|--------------------------|------------------------------|----|----------------------|-----|
| Ammonia | Heated Drums or ISO tank | ISO tank supply to vaporizer | | On Site Purification | |
| Nitrogen | Liquid Nitrogen | | | On Site Generator | |
| Hydrogen | Compressed Gas Trailer | Electrolyzer | | On Site Generator | |

Table 3. Table 3 shows gas delivery schemes that can meet both flow and purity specifications that are available to customers today, and their applicability to LED fab scale.

source. Above 100 to 150 Nm³ per hour flow, tube-trailer supply tends to be uneconomic simply due to the logistic costs and frequency of trailer changes required. For large scale fabs, with 25-50 tools, on-site hydrogen generation becomes the most cost effective supply mode, either by electrolysis of water, or by modular packaged steam methane reformer, providing 100 to 1000 Nm³/hour at 99.999 purity from natural gas feedstock.

New Challenges

Gas suppliers are evolving from being "traditional suppliers" to becoming integral parts of the manufacturing industry as PV and high-brightness LED manufacturers seek strong, reliable and knowledgeable partners with expertise in the wide range of specialist materials used in these highly complex and multi-stage production processes. As the PV and HB-LED industries grow, other challenges for manufacturers will include

managing safety and environmental issues, and developing materials technology that will both reduce costs further and increase cell and LED chip efficiency. **G&I**

For more information, please see <http://www.linde-gas.com/electronics>

DR. ANISH TOLIA IS HEAD OF MARKET DEVELOPMENT, GLOBAL SEMICONDUCTOR, LED AND AMERICAS FOR LINDE ELECTRONICS. HE IS RESPONSIBLE FOR GLOBAL STRATEGY AND MARKET DEVELOPMENT FOR THE SEMICONDUCTOR AND LED SECTORS AS WELL AS MARKET DEVELOPMENT FOR NORTH AND SOUTH AMERICA. DR. TOLIA JOINED LINDE IN NOV 2007. PRIOR TO JOINING LINDE, DR. TOLIA HAD A CONSULTING PRACTICE WHERE HE ADVISED CORPORATIONS AND PRIVATE EQUITY INVESTORS ON MARKETS AND TECHNOLOGIES IN SEMICONDUCTOR, SOLAR AND FLAT PANEL INDUSTRIES. DR. TOLIA HAS ALSO SPENT SEVERAL YEARS AT LEADING EQUIPMENT COMPANIES SUCH AS APPLIED MATERIALS AND PHOTON DYNAMICS (NOW ORBOTECH) IN VARIOUS



TECHNICAL AND MARKETING ROLES. DR. TOLIA HAS BEEN GRANTED OVER 10 US PATENTS AND HOLDS A PH.D. IN CHEMICAL ENGINEERING FROM PURDUE UNIVERSITY. HE CAN BE REACHED AT ANISH.TOLIA@LINDE.COM