Reducing cost per watt through innovative gas and chemical technology.

Linde in Solar.
The Linde Group is a world leader in industrial gases and engineering with more than 50,000 employees working in approximately 100 countries worldwide.

Linde’s comprehensive portfolio of industrial gases and chemicals, combined with its reputation for technology and global execution makes Linde the partner of choice for manufacturers who value excellence - in virtually every global industry. In the clean energy field, with its unique gas and engineering capability and global footprint, Linde is at the forefront of the emerging hydrogen economy, active in CO2 capture and storage, and leading the development of innovative waste-to-energy schemes. In solar energy Linde supplies materials to more than half of the major solar cell manufacturers worldwide.

Serving you, wherever you are.
Linde Electronics, part of The Linde Group Gases Division, is a leading global supplier to the solar cell, semiconductor, flat panel display, and electronic packaging industries. Our mission is to enable smarter, lower cost and more sustainable electronics manufacturing through innovative technologies and solutions.

Linde’s global reach – operating in more than 100 countries - gives you unparalleled access to our wide range of capabilities, which include:

- Global supply of critical materials and services
- Innovation in gas and chemical based solutions
- Engineering turnkey solutions
- Lowering emissions
- Environmentally sustainable manufacturing
- Reducing manufacturing costs and improving yields

Linde’s solar experience is second to none, with crystalline and thin film Si customers in every major manufacturing geography.
An integral part of the PV manufacturing industry.

Although less than 25 different gases and chemicals are used in solar-cell manufacturing, in comparison with more than double that amount for semiconductors, the volumes required are significantly greater and supply chain management presents unique challenges. Amongst the direct materials for thin film Si in particular, glass and gases together can account for about 40% of the cost of solar module production. Thus while a 100MW facility requires significant investment in infrastructure to ensure continuity of material supply, a 1GW facility requires the entire output of an industrial scale production facility for several of the principal materials.

Delivering Safely
Linde has a strong track record in the safe manufacture, handling and distribution of the specialist products needed for solar cell manufacture, as well as in the design and installation of the gas and chemical systems necessary for safe use. Linde has more than 10 years experience in both the supply of bulk silane and the design and operation of on-site fluorine generators, with more than 30 bulk silane and 25 fluorine systems in use at customer sites worldwide.

We work in partnership with our customers and contractors to ensure projects are delivered safely. Our structured approach to risk mitigation includes:

- HAZOP (Hazard & Operability Studies) & Design Reviews
- FMEA (Failure Mode Effects Analysis)
- PSR (Project Safety Reviews)
- Product stewardship / New Product Introduction Process

Linde’s global footprint and well established culture of best practice transfer is ideally suited as the PV industry sets up large scale manufacturing in new geographies. For example, when Moser Baer constructed the world’s first industrial scale thin film Si PV plant in India, Linde’s global PV experts teamed with colleagues at Linde’s large Indian operation to ensure a world class project implementation and a smooth start-up of this pioneering project.
Our mission is to develop and apply advanced gas and chemical technologies.

Linde’s mission is to develop and apply advanced gas and chemical technologies that help solar cell manufacturers move toward grid parity, while encouraging the adoption of environmentally sustainable manufacturing.
In order to reduce the cost per watt, Linde has moved from ‘traditional supplier’ to becoming an integral part of the photovoltaic industry. Linde’s people understand the critical manufacturing processes and are developing innovative gas and chemical technologies to lower the overall cost per watt. These cost reduction technologies will have increasing impact as the industry moves to ever larger manufacturing scale.

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 Vapor Deposition (PECVD) system. The result is a thin film of silicon on the 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 (B₂H₆), phosphine (PH₃) and methane (CH₄).

This process also results in silicon deposition on other surfaces in the process chamber such as the showerhead and chamber walls, which must be periodically cleaned. Typically a fluorine-based etch process using NF₃, SF₆ or F₂ is employed for this purpose.

Nitrogen is a critical utility in thin film Si fabs and is used for multiple tasks including purging vacuum pumps and dilution of toxic or flammable gases in chamber exhaust lines for safety.

Another important step 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).

Gas cost reductions are possible by a variety of methods, such as:

**On site generation of bulk gases**
The economics of large scale fabrication plants favour on site generation of major bulk gases such as hydrogen and nitrogen. This eliminates the transportation and delivery cost of cylinders and enhances security of supply.

**Lowering Cleaning Costs**
More than 50% of the capital cost and over 40% of the direct materials cost is consumed in the PECVD processes that deposit the active silicon layers. The PECVD chambers require frequent cleaning of silicon residue. Replacing current methods (NF₃ or SF₆) by fluorine (F₂) can improve cleaning economics by up to 40%. Fluorine is generated on-site using packaged fluorine generators.

**Increasing Throughput**
By utilizing fluorine based cleaning the throughput of the PECVD process may be increased by up to 6% at no extra cost. Additives in silane may increase deposition rates and thereby increase throughput.

**Improving cell efficiency**
The cell efficiency is strongly affected by the composition of the active p-i-n layers in the amorphous and microcrystalline steps. The cell efficiency may be improved by controlling critical impurities in the precursor gases.

Linde’s PV technology development roadmap targets each of these areas, and many more. In every case, Linde’s approach involves close collaboration with key members of the technology value chain, including suppliers, PV equipment manufacturers and customers. This close integration with the industry and alignment of research and development goals with the primary objective of reducing cost per watt have been critical factors in convincing more than half of all thin film Si manufacturers globally that Linde is the gas partner of choice for them.
Solar Thin Film Fabrication Plant Overview.

On-site fluorine generation

Compressed dry air systems

Turnkey engineering and on-site gas and chemical management

Cylinder gases
Halocarbon 14
Oxygen
Dopants
Gas distribution and monitoring
Gas cabinets
VMBs
Gas analysers and purifiers
Pipework systems

On-site gas generation
Nitrogen
Hydrogen

Bulk liquified gases
Nitrogen
Hydrogen
Argon

Bulk compressed gases
Hydrogen
Helium
Nitrogen trifluoride
Silane
The industry continues to build capacity and make advances in crystalline silicon.

Crystalline silicon solar cells are currently used in more than 80% of worldwide solar installations. Applications are primarily consumer based (on-grid) installations, but also provide a flexible means of supporting underdeveloped (off-grid) locations where grid power is unavailable. Crystalline silicon cell output is expected to continue to grow at 20-30% year on year for the next several years.

Silicon cost represents 60% of the overall c-Si cell manufacturing costs, although this is expected to decline as new global Si capacity comes on stream. The process materials component cost (7%) plays a critical role in enabling higher cell efficiencies and lower production costs.
Linde provides a full product portfolio of high purity bulk and specialty gases as well as wet chemicals for c-Si cell processing. Linde has the experience and expertise to optimize such critical c-Si process steps as etch/texturization, doping, PSG removal, edge isolation, anti-reflective coating (ARC) deposition, and various cleaning steps that are essential in c-Si cell performance.

Cost reduction
Linde has demonstrated capabilities and technologies to provide recycling and/or reuse of selected waste in-process chemistries. We work closely with PV cell manufacturers to develop specific systems that can reduce the expenses associated with chemical waste management, and environmental impact. Such systems enable further reductions in operational costs for our customers. One example of this is our KOH recycling capability which is detailed on page 15.
Linde supplies the full range of gas and chemical products necessary for PV manufacture†

Typical gas and chemical requirements for thin film and crystalline Si manufacture. Exact requirements will vary depending on the process.

**Thin film Si**

<table>
<thead>
<tr>
<th>Product</th>
<th>Typical Grade</th>
<th>Typical Package (&lt;200MW)</th>
<th>Typical Package (&gt;200MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane (SiH₄)</td>
<td>Electronic</td>
<td>Cylinder bundle / ISO module (6000kg)</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Nitrogen trifluoride (NF₃) *</td>
<td>Electronic</td>
<td>Cylinder bundle / ISO module (8000kg)</td>
<td>On-site plant</td>
</tr>
<tr>
<td>Fluorine (F₂) *</td>
<td>Electronic</td>
<td>On-site plant</td>
<td>Liquid tank / on-site plant</td>
</tr>
<tr>
<td>Sulphur hexafluoride (SF₆) *</td>
<td>Electronic</td>
<td>Liquid tank / Tube trailer** / Liquid tank / On-site plant / Pressure tank / Tube trailer**</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>Electronic</td>
<td>Cylinder</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Liquid tank / Liquid tank / Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Trimethylboron (TMB) mixtures</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Phosphine (PH₃) mixtures</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Ethylene (C₂H₄)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Dimethyl ether (C₃H₈O)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Acetic acid (CH₃COOH)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Sodium Hydroxide (NaOH)</td>
<td>Electronic</td>
<td>Cylinder / Liquid tank / Drum / ISO module (20,000kg)</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Custom Product Mixes Available</td>
<td>per specification</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**c-Si**

<table>
<thead>
<tr>
<th>Product</th>
<th>Typical Grade</th>
<th>Typical Package (&lt;500MW)</th>
<th>Typical Package (&gt;500MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane (SiH₄)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Tetrafluoromethane (CF₄)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Nitrous Oxide (N₂O)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Acetic acid (CH₃COOH)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Ethanol (C₂H₅OH)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Hydrofluoric acid (HF)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Isopropyl alcohol (C₃H₈O)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Potassium Hydroxide (KOH)</td>
<td>Electronic</td>
<td>Cylinder / Cylinder bundle / Tonne tank</td>
<td>ISO module (6000kg)</td>
</tr>
<tr>
<td>Nitric acid (HNO₃)</td>
<td>&lt;10 ppb *</td>
<td>200L drum / 1m³ tote</td>
<td>1m³ tote / ISO tank **</td>
</tr>
<tr>
<td>Phosphoric acid (H₃PO₄)</td>
<td>&lt;10 ppb *</td>
<td>200L drum / 1m³ tote</td>
<td>1m³ tote / ISO tank **</td>
</tr>
<tr>
<td>Sulfuric acid (H₂SO₄)</td>
<td>&lt;10 ppb *</td>
<td>200L drum / 1m³ tote</td>
<td>1m³ tote / ISO tank **</td>
</tr>
<tr>
<td>Sodium Hydroxide (NaOH)</td>
<td>&lt;10 ppb *</td>
<td>200L drum / 1m³ tote</td>
<td>1m³ tote / ISO tank **</td>
</tr>
<tr>
<td>Custom Product Mixes Available</td>
<td>per specification</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Linde supplies the full range of gas and chemical products necessary for PV manufacture

Bulk gases
Linde delivers secure and reliable supply of essential bulk gases, such as nitrogen, oxygen, argon, hydrogen and helium to both thin film Si and c-Si customers alike. These products are manufactured by our global network of high purity gas plants and delivered by road in liquid or compressed form to storage facilities on the customer site. Linde offers 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.

On-site nitrogen & hydrogen generation
For large gas consumption, Linde’s ECOVAR systems offer a low cost, reliable solution for nitrogen, oxygen, hydrogen and compressed air. On-site supply systems are built around standardized components to ensure maximum cost efficiencies, and can be designed for year round uninterrupted supply (8760 hours) through incorporation of redundancy. Systems are automatically controlled, and are monitored by the nearest Linde Gas facility to ensure a reliable gas supply.

On-site fluorine generation
Linde’s recommended alternative to global warming gases for chamber cleaning, fluorine (F₂), is also generated on-demand on customer sites, utilising modular Generation-F® systems that enable capacity scaling as PV plants ramp. High purity fluorine gas is the highest performance cleaning gas available, improving productivity on CVD tools, reducing energy consumption and environmental impact, with zero Global Warming Potential. Linde has years of unrivalled experience in the safe and reliable generation and delivery of fluorine, to the exacting specifications of the display and semiconductor industry. Systems are available to supply the cleaning gas needs of any size thin-film PV production fab, from 1 tonne to hundreds of tonnes per year.

Special Gases
Linde offers the full range of special gases to support photovoltaic manufacture. Linde operates a global network of 8 electronic special gas production plants strategically located in key markets, linked with 20+ local stock locations by a state-of-the-art global logistics capability. Electronic special gases, including silane, NF₃, ammonia and dopant mixtures, are shipped in a variety of container sizes depending on application, ranging from individual cylinders, to ISO containers.

Chemicals
AUECC, a Linde Group company is a leading supplier of wet process chemicals to all high technology industries in Asia and beyond. Manufacturing is located in Shanghai, China and Taiwan. Linde provides a full range of acidic, alkaline, and organic process chemistries for monocrystalline and polycrystalline PV processing applications from silicon manufacturing through cell fabrication. Linde’s products support the PV wet process solutions for Saw Damage Repair, Surface Texturization, Surface Cleaning and PSG and Edge Isolation Removal.
Turnkey engineering and on site gas and chemical management.

Linde has installed hundreds of safe, efficient and robust gas systems within the global semiconductor, TFT-LCD, solar and LED industries. Linde’s expertise includes consulting, process design, turn-key project management, and commissioning.

For on-going systems and materials management, Linde Electronics can offer full on-site gas and chemical management services, giving you full time access to in-depth gas and chemical know-how which ensures a safe and smooth operation with minimised downtime and risk. Linde currently operates on-site teams at more than 50 customer sites worldwide.
Facing environmental challenges and enabling sustainable manufacturing.

A clear focus on environmentally sustainable manufacturing is a pillar of the Linde Group philosophy, and it is our goal to enable improvements in sustainability in every industry we serve. In the solar industry we can provide real solutions to reduce your CO₂ footprint and recycle valuable consumables. In the area of chamber cleaning for the very large area PECVD tools, gases like NF₃, which are consumed in significant volumes, have some of highest Global Warming Potentials (GWPs) measured. In the case of NF₃, approx 1,000kg of gas is consumed per MW of module manufacturing every year, regardless of technology provider. One of the highest priorities for Linde’s R&D programme in solar has been to pioneer technologies to prevent these gases being released into the atmosphere – either through recycling or through alternative applications using environmentally less harmful gases.

NF₃ replacement
Linde has pioneered the use of molecular fluorine (F₂) as a replacement for NF₃ and SF₆ in PECVD chamber cleaning. While NF₃ and SF₆ are high GWP gases, F₂ has zero global warming impact. Replacing NF₃ with Fluorine in a 1GW thin film Si fab would result in elimination of NF₃ consumption with an untreated global warming potential equivalent to nearly 17 million tonnes of CO₂ per year. Linde’s proven technology for generating F₂ on-site and on-demand eliminates the need for large volume storage and addresses all the safety requirements for handling this reactive material. In addition to its environmental benefit, F₂ reduces the time for chamber cleaning, thereby increasing plant productivity, through a more efficient etching process.

KOH Recycling
Through the Linde Group subsidiary, AUECC, based in Taiwan, Linde offers end to end recycling of waste KOH for applications in mono-Si cell processing. Via a unique reprocessing technology, KOH recycling yields product purity equal to, or even better than, original ‘fresh’ KOH quality. This innovative technology is available on-site, anywhere in the world. Cost saving aspects include reduced waste neutralization chemicals costs, reduced municipal waste effluent sewerage costs, reduced fresh purchases of potassium hydroxide, reduced freight expenses for fresh KOH deliveries and reduced operator handling expenses. Overall estimated savings are between 20-30% compared with the continued purchase of fresh KOH.

Technology development
Linde, the leading supplier of gases, also takes leadership in solar PV research and development to drive down the cost per watt in solar PV manufacturing. Linde has solar research and development locations in San Marcos, California and in Europe with a joint development partner. Linde’s research and development efforts encompass both thin-film and crystalline silicon cell manufacturing. Areas of focus include developing products and services that capitalise on efficiencies of scale, improve solar cell performance, optimise process and film parameters and develop new, novel materials that drive down costs.
Leading. Linde Electronics is part of the Linde Group, the leading gases and engineering group of companies with almost 50,000 employees working in approximately 100 countries worldwide.

Linde’s mission is to enable smarter, lower cost and more sustainable electronics manufacturing through innovative technologies and solutions.

We believe in the concept of zero accidents and incidents, striving to create a safe and effective working environment for our people and our customers.

We wish to ensure long term customer satisfaction and loyalty by consistently providing products and services that meet each customer’s expectations for quality.

We develop and promote technologies, products and services that are environmentally sustainable.

To find out more about Linde Electronics, visit us online or send us an email:

electronicsinfo@linde.com

North America
North America (Linde) +1 (0)908 329 9700
+1 (0)800 932 0624

Asia
China (Linde Lien Hwa) +86 (0)21 6105 9888 ext 9456
India (BOC India) +91 (0)99 7460 3377
Korea (Linde) +82 (0)2 780 9331
Malaysia (MOX-Linde) +60 (0)379 554 233
Philippines (Linde Philippines Inc.) +63 (0)2 702 7500
Singapore (Linde Gas Singapore) +65 (0)6861 3678
Taiwan (BOC Lien Hwa) +886 (0)2 2786 6000
Thailand (Thai Industrial Gases) +66 (0)2 338 6253

Europe & Middle East
France (Linde) +33 (0)4 72 47 66 10
Germany, Continental Europe & Middle East (Linde) +49 (0)89 7446 1122
Greece (Linde Hellas) +30 (0)21 110 45 000
Italy (Linde Gas Italia) +39 (0)029 037 31
Spain (Linde) +34 (0)687 927 430
Switzerland (PanGas) +41 (0)844 800 300
United Kingdom & Ireland (BOC) +44 (0)800 02 0800

For all regions not listed, please refer to www.linde-gas.com/electronics or contact us at electronicsinfo@linde.com