Climate-friendly thin-

Text: Michael Matz

A new study suggests that fluorine gas is a compelling alter trifluoride, a potent greenhouse gas widely used by thin-film for PECVD chamber cleaning

Highlights

- In September, Linde and Malibu published the results of several months of experiments on fluorine-based plasma-enhanced chemical-vapor deposition chamber cleaning at Malibu's development facility
- Fluorine demonstrated a chamber cleaning rate 2.7 times that of NF_3, and yielded identical cleaning results and module performance
- The use of fluorine can reduce cleaning time by more than 50 percent and boost line throughput by as much as 10 percent, according to Linde
- Linde says that increased productivity from fluorine usage can translate into a €1.2 million ($1.8 million) annual cost of ownership benefit for a single-tandem line and a €2.9 million ($4.2 million) benefit for a double-tandem line

The thin-film silicon PV industry may be able to breathe a collective sigh of relief. New research suggests that the use of fluorine gas offers an economically viable alternative to nitrogen trifluoride (NF_3) in the cleaning of plasma-enhanced chemical-vapor deposition (PECVD) chambers. What's significant about this finding is that NF_3, which is widely used in the thin-film industry for PECVD cleaning, is a greenhouse gas with a global warming potential 16,800 times that of carbon dioxide (CO_2) over a period of 100 years (see PI 12/2008, p. 102). Fluorine gas (F_2) has zero global warming potential and thus holds great promise to boost the environmental record of thin-film silicon producers – assuming it is an effective cleaning agent.

The research paper, presented by gas producer Linde AG and thin-film company Malibu GmbH & Co. KG at the European Photovoltaic Solar Energy Conference (EU PVSEC) in Hamburg, Germany, in September, showed not only that fluorine works as a cleaning agent, but that it also works more quickly. According to the results, F_2 demonstrated a cleaning rate nearly three times that of NF_3, and delivered identical cleaning results and module performance. Linde says that the faster cleaning rate translates into a 4-percent productivity improvement for thin-film production lines. According to calculations provided by the company, the increased productivity could yield a €1.2 million ($1.8 million) annual cost of ownership benefit for a 60 MW line and €2.9 million ($4.2 million) for a 120 MW line.

Cleaning and climate

Thin-film silicon solar cell production facilities use PECVD chambers to deposit silicon layers on substrates. Over time, silicon deposits build up on chamber walls, increasing the risk of particles falling onto the modules and lowering their efficiencies. It is thus crucial for producers to regularly clean silicon deposits from these chambers. Cleaning processes commonly use gas containing fluorine, like NF_3, which provide free fluorine radicals to volatilize deposits. But the high global warming impact of such gasses means that any amount that escapes into

SCHÜCO International KG

Clean production: Malibu, which manufacturers amorphous silicon modules, uses an environmentally friendly solution to clean its deposition equipment. Back in June, Malibu partners - Eon's Wulf Bernotat and Dirk Hindrichs from Schüco – seemed happy with their new investment.

film PV

native to nitrogen
silicon producers

the atmosphere can significantly decrease the positive clean energy impact of PV modules.

Scrutiny regarding the impact of NF_3 is growing. According to research by the Scripps Institution of Oceanography published last October, about 16 percent of the NF_3 manufactured globally escapes into the atmosphere – most likely because it doesn't get abated. The same study estimated that the NF_3 level in the atmosphere increases by 11 percent annually. In April, the US Environmental Protection Agency released a draft rule that would impose strict monitoring and reporting requirements for greenhouse gas usage (including NF_3) on US electronics and PV manufacturers, among other industries. The comment period for this rule ended in June, so it's possible that the final rule will be promulgated in November ahead of the Copenhagen negotiations.

Linde's Paul Stockman says that an instructive way to look at the environmental impact of NF_3 usage in thin-film production is carbon payback time, or the number of years it takes for the greenhouse gas emissions saved by PV module production to offset the emissions associated with the PV manufacturing process. According to his own calculations, the carbon payback time just for the use of NF_3 in PECVD cleaning is 1 to 3 years of module operation, depending on where the modules are deployed and what the electricity mix is in that location.

Fluorine experiments at Malibu

Since 2008, Linde has had a joint development program with

▲ Faster and eco-friendlier: Linde's Generation-F line of on-site fluorine generators allows thin-film PV makers to produce climate-friendly fluorine gas as needed to clean PECVD chambers. The company's joint study with Malibu revealed that fluorine gas has a significantly faster cleaning rate than NF_3, which is currently the most commonly used cleaning gas in the industry.

Malibu, which is a German joint thin-film PV venture of energy company Eon AG and Schüco International KG, a building materials firm and solar integrator. According to Stockman, in February, Linde installed an on-site fluorine production unit at Malibu's R&D lab. The company operates a 40 MW amorphous silicon thin-film facility in Bielefeld, Germany. Over several months, the partners conducted experiments on the cleaning performance of the device and published the results in the paper presented at EU PVSEC.

The cleaning experiments used a Linde Generation F-80 fluorine generator and one chamber of an Applied Materials AKT PECVD unit for Gen 5 modules (1,300 × 1,100 mm). On the way to the PECVD chamber, fluorine gas passed through a remote plasma source, which is a box – typically situated on top of the chamber – used to dissociate the gas into plasma.

The main experimental finding – that F_2 demonstrated a cleaning rate 2.7 times that of NF_3 – has to do with differences in the bond strengths of the two molecules. F_2 has much weaker bonds than NF_3, which means more F_2 can be dissociated into fluorine atoms per unit of energy, yielding a greater flow of atomic fluorine into the PECVD chamber. Because the fluorine atoms do the cleaning work, greater atomic fluorine flow means a faster cleaning rate. According to Stockman, the study also indicated that F_2 could potentially achieve a cleaning rate as much as 6.4 times the cleaning rate of NF_3, depending on the working set-up. The size of the mass flow controller in the experimental set-up limited the flow of fluorine atoms, effectively capping the cleaning potential of fluorine gas.

Because of the faster cleaning rate, Linde says that the use of F_2 can reduce cleaning time by more than 50 percent and thereby boost line throughput by as much as 10 percent. Given that PECVD cleaning can be a bottleneck in the thin-film production line, the faster throughput at this stage can translate into a significant cost of ownership benefit, according to Linde. The company has provided PHOTON International with calculations of this benefit (see table, p. 129), though it wouldn't provide details for its fluorine generator or gas prices. Thus, these cost of ownership calculations have to be taken with a degree of caution. However, Linde says these numbers are based on average productivity improvements it observed when testing on-site fluorine generators on machinery from different equipment manufacturers.

Linde touts another advantage of fluorine over NF_3: reduced materials usage. Since the nitrogen in NF_3 does not contribute to the cleaning, molecular fluorine requires 20 percent less mass than NF_3 to yield the same quantity of atomic fluorine radicals. That means 80 kg of F_2 can achieve the same amount of cleaning as 100 kg of NF_3. According to the calculation provided by Linde, the lower requirement of materials could translate into a €480,000 ($701,900) annual cost of ownership benefit for a 60 MW production line and a €1.6 million ($$2.3 million) benefit for a 120 MW line. Additionally, because it takes less energy to create fluorine atoms from fluorine gas, the gas has the benefit of reduced power consumption compared to NF_3. Linde claims a 60 percent reduction in power consumption by the remote plasma source.

After 4 months of experimentation with F_2 cleaning, the researchers found »no signs of degradation« or particle accumulation in the chamber. Finally, they compared the performance of the modules produced with F_2- and NF_3-based cleaning, and no difference was observed in the IV curves.

Fluorine as you need it

Fluorine gas is climate-friendly, but it is also a highly reactive and toxic element. As a result, there are significant handling and distribution risks associated with the use of high-pressure cylinders of F_2. To address these risks, Linde offers a line of on-site fluorine generators, called Generation-F, designed for PECVD chamber cleaning. On-site fluorine generators allow manufacturers to produce fluorine gas as it

Linde's cost of ownership calculation for NF_3 replacement with F_2

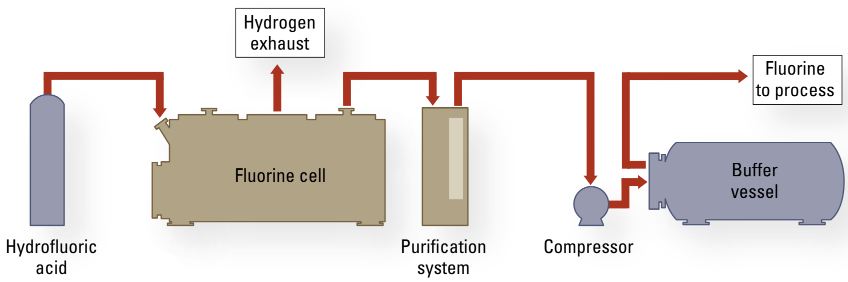
		Single-tandem line	Double-tandem line
Cleaning requirements	Line size	60 MW/yr	120 MW/yr
	NF_3 consumption	80,000 kg/yr	160,000 kg/yr
	F_2 mass reduction factor	0.8	0.8
	F_2 consumption for equal throughput	64,000 kg/yr	128,000 kg/yr
Productivity benefit	Productivity improvement	4%	4%
	New line output	62.4 MW/yr	124.8 MW/yr
	Selling price per W	€1.50 ($2.19)	€1.50 ($2.19)
	Manufacturing cost per W	€1 ($1.46)	€0.90 ($1.32)
	Profit per W	€0.50 ($0.73)	€0.60 ($0.88)
	Value of extra throughput	**€1.2 mn ($1.8 mn)**	**€2.9 mn ($4.2 mn)**
Mass reduction benefit	NF_3 price/kg	–	–
	Fluorine price/kg	–	–
	Annual NF_3 cost	–	–
	Annual fluorine cost	–	–
	Material cost saving	**€480,000 ($701,900)**	**€1.6 mn ($2.3 mn)**
Overall annual benefit		**€1.7 mn ($2.5 mn)**	**€4.5 mn ($6.6 mn)**

source: Linde Electronics

▲ Cost of ownership benefit? According to numbers provided by Linde, the improved productivity and reduced materials requirement associated with fluorine-based cleaning can yield an overall annual benefit of €1.7 million ($2.5 million) for a 60 MW production line and €4.5 million ($6.6 million) for a 120 MW line. But the numbers have to be read with caution, as Linde wouldn't provide prices for gasses or the reactor.

▶ Linde's fluorine generators use electrolysis to produce fluorine gas from hydrofluoric acid. The gas is purified, compressed, buffered and then sent to the cleaning process.

Process flow diagram for on-site fluorine generation



is needed, thereby limiting the amount of the substance that is present at any given time. Any fluorine gas that is present is held at low pressure, reducing its reactivity. The company has been supplying these systems to the electronics industry for more than 10 years and is now eyeing new customers in the thin-film PV industry.

On-site fluorine generators employ an electrolytic decomposition process to convert a feedstock of anhydrous hydrofluoric acid into molecular fluorine gas. Linde's fluorine generators are integrated with a purification system, compressor and buffer unit (see diagram, p. 129). The purification unit is proprietary Linde technology that removes trace amounts of hydrofluoric acid and other impurities, and produces a grade of fluorine gas that is more than 99.9 percent pure. The compressor maintains the gas at an operating pressure of 2.5 atmospheres – or about 10 percent of the typical pressure of bottled fluorine. Since the reactivity of fluorine increases with pressure, Linde's system takes away much of the reactivity, according to Stockman. »We're raising the pressure just enough above atmospheric pressure to drive the process,« he says. The buffer unit is sized to allow for continuous generation of F_2 for processes with varying demands for cleaning gas.

The fluorine gas generation systems have additional safety features to address the toxicity and reactivity of fluorine gas. All fluorine gas that is above ambient pressure is protected under double containment. The generation equipment has ventilated enclosures around all the components. Fluorine gas is transported from the generator to the cleaning site through double-contained lines. The gas passes through the inner line, and the outer line is filled with pressurized nitrogen. Pressure monitors are used to detect breaches in the fluorine line. Stockman says that over the past 10 years, his company has supplied more than 30 on-site fluorine generators to display and semiconductor manufacturers with no safety incidents.

Besides Malibu's development facility in Bielefeld, Linde is currently installing a commercial-scale fluorine gas system at Malibu's manufacturing plant in Osterweddingen, Germany, says Stockman. The plant will come on line in the first quarter of 2010. Stockman could not divulge names of potential client companies besides Malibu, saying only that »We've been talking with end-users and original equipment manufacturers on different platforms.«

Equipment manufacturing companies Oerlikon and Applied Materials are looking at the F_2 alternative because their equipment would have to be adapted, says Mariska de Wild-Scholten of the Energy Research Centre of the Netherlands (ECN). While neither company would comment on the issue, Linde's Stockman says that his company consulted with both Oerlikon and Applied Materials for the experimental trials and they have been »participatory in some places.« Claims Stockman: »They want to make sure they have, available to their customers, saleable solutions that their salespeople can respond to immediately.«

It might even be true that this is more than wishful thinking on the side of a salesman. At least, Pramac Swiss SA, which just started production using NF_3 to clean its Oerlikon reactors, says F_2 »is the only possible alternative to NF_3 in order to significantly reduce the cost of ownership.« And its operations manager Massimo De Rossi has always been aware of that fact. Its plant has even been built with a foreseen area for on-site F_2 generation, Pramac says. The reason it has not been implemented yet? First, the »process is not fully qualified by Oerlikon,« and second »there are too many safety measures to be carried out in order to make the system acceptable for local authorities,« adds De Rossi.

Malibu apparently didn't have those acceptance problems for their factory in Osterweddingen. And its supplier, Applied Materials, reported F_2-cleaning as an option in our market survey on PECVD systems for silicon absorber deposition (see article, p. 190). The other choice Applied Materials offers for cleaning – which is also NF_3-free – is a mechanical solution. ●