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Volume 38 Issue 2 2016

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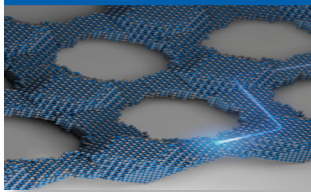
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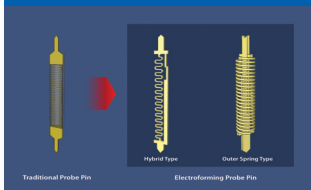
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# On-site generated fluorine

High-speed chamber cleaning with zero global warming potential

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# On-site generated fluorine:

## Effective, safe, and reliable source of fluorine for electronics for over 15 years

On-site fluorine generation has proven a safe alternative to greenhouse gases often used in electronics manufacturing. Linde delves into its makeup, history, and how fluorine is effectively used to clean CVD chambers and in many other applications.

By Dr. Paul Stockman, Head of Market Development, Linde Electronics

ON-SITE GENERATED FLUORINE ( $F_2$ ) is a safe and reliable alternative to greenhouse gases for chemical vapor deposition (CVD) chamber cleaning and is currently used in the commercial production of semiconductors and LCD screens in multiple sites in Asia and Europe. In the first of a two-part series, we describe the on-demand production of high-purity fluorine as demonstrated by Linde's installed base of more than 30 generators serving global industries over 20 years and electronics manufacturers for more than 15 years. Production capacities ranging from 1 to 100+ tons / year have displaced high-pressure fluorine cylinder and bulk nitrogen trifluoride ( $NF_3$ ) supplies. Certification by leading safety and engineering authorities document the design details required to effectively deliver fluorine reliably and safely without incident. In Part 2, we will describe the fundamental physical properties of fluorine, which are the basis for significant process and cost of ownership improvements and which eliminate the need for greenhouse gases in chamber cleaning.

### History of fluorine

Fluorine was first produced and isolated by the French chemist Henri Moissan in 1886. However, the challenges in production processes and the element's vigorous reaction chemistry limited its use to bench-scale apparatuses for small experimental quantities. Industrial-scale production technology was first developed for the Manhattan Project in 1943 when gas-phase uranium hexafluoride ( $UF_6$ ) was identified as the preferred method for separating the fissionable  $^{235}U$

isotope from the remaining 99 percent of isotopes. After the war, fluorine production technology was further developed and proliferated with the spread of independent nuclear materials capability and from this base further non-nuclear applications were developed.

Today, tens of thousands of tons of industrial fluorine are produced commercially all over world as chemical feedstock for organic fluorides and various inorganic fluorides such as  $SF_6$ ,  $NF_3$ , and boron trifluoride ( $BF_3$ ). Additionally, industrial fluorine is used for chemical modification of surfaces and to make certain plastics impermeable to water, oxygen, and hydrocarbons.

While industrial fluorine can be transported in large volumes either as a cryogenic liquid or as a compressed gas, safety and logistic concerns dictate that most fluorine is produced and consumed on-site and on-demand at low or atmospheric pressure. This limits both absolute inventory of fluorine, because it is only made as is needed, and also prevents high-energy, high-pressure events because the reactivity of fluorine is directly related to its pressure.

### How fluorine is produced

Fluorine is produced by electrolysis of anhydrous hydrogen fluoride (HF) to yield hydrogen ( $H_2$ ) gas at the cathode and  $F_2$  gas at the anode; the amount of gas evolved is directly proportional to the current applied. The process is similar to the electrolysis of water to produce  $H_2$  and oxygen ( $O_2$ ); however,

it requires the salt potassium bifluoride ( $\text{KHF}_2$ ) as a charge carrier and transport medium. The HF consumed by electrolysis is replaced by adding HF gas or HF liquid directly to the salt-acid mixture, with an effective composition of  $\text{KHF}_2 \cdot (\text{HF})_{x=1}$ , which melts at  $72^\circ$  Celsius. The electrodes are physically separated to prevent the rising  $\text{H}_2$  and  $\text{F}_2$  gas bubbles from recombining, and the gases are evolved over the melt and collected through separate vents. Material selection of electrode and cell body components is essential to ensure a long operating lifetime of the fluorine cell with minimum maintenance requirements, and periodic chemical analysis of the salt-acid mixture verifies the integrity of components.

HF dissolved in the molten  $\text{KHF}_2$  salt is electrolyzed to produce  $\text{H}_2$  at the cathodes and  $\text{F}_2$  at the anodes. The  $\text{HF}_2$  feed can be introduced either as a gas or a liquid. The evolved streams of both  $\text{H}_2$  and  $\text{F}_2$  contain 1-5 percent of HGas as a vapor-phase impurity. The  $\text{H}_2$  stream is diluted to concentrations below the LEL (lower explosion limit) of 4 percent and scrubbed before being vented to atmosphere. For high-purity applications, the fluorine stream is purified to remove the HGas as well as other low-level impurities. Compression to a working pressure of 1.0 to 1.5 barg and buffering in a temporary tank provides an adequate process supply at constant pressure without creating excess inventory.

Anhydrous HF, either in gas cylinders or larger bulk containers, is used to feed the fluorine cell. The  $\text{H}_2$  byproduct is extracted for disposal, while the generated fluorine is further purified before being compressed to 1 to 1.5 barg and temporarily buffered before use in the customer process. All key process modules are enclosed in extracted cabinets as part of the safety design.

**On-site fluorine generators**

Concerns for safety and reliability have informed the design of on-site fluorine generators for use in the high-tech thin-film industries of semiconductor, display, and photovoltaic manufacturing. As with any chemical introduced into these market sectors, safety risks need to be identified and mitigated. Fluorine is the most electronegative element from the periodic table and this extreme reactivity is the cause for risks to both health and equipment.

Fluorine falls in the middle of the spectrum of the many toxic gas-phase chemicals commonly used in thin-film device manufacturing, a few examples of which are shown in Table 1 [Reference: *American Conference of Governmental Industrial Hygienists*]. Mitigation strategies focus on three areas: material selection and passivation, containment, and design for minimal inventory.

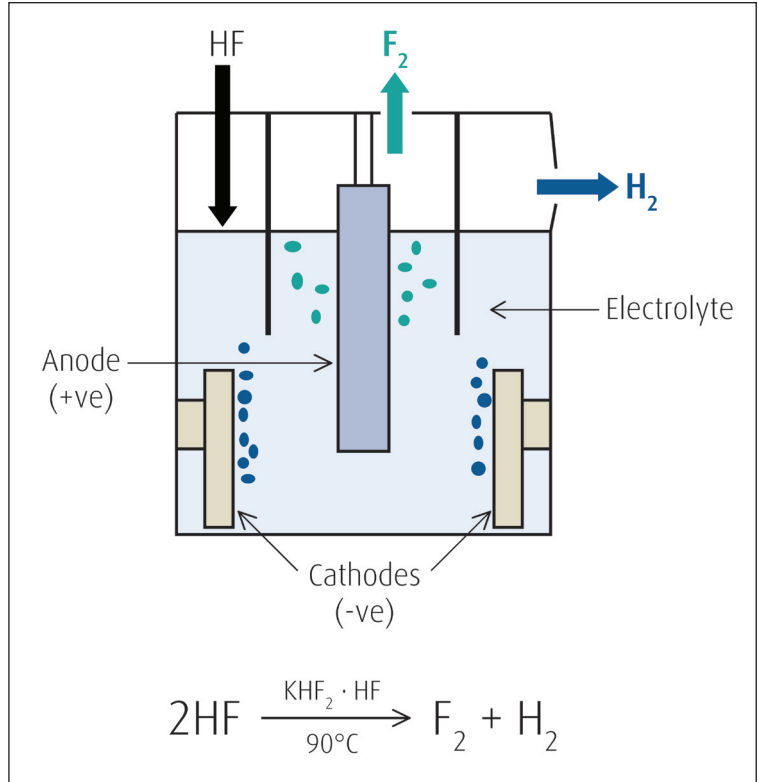


Figure 1: Electrolytic production of fluorine

**Comparison of toxicity of electronic gases**

Gas TLV/TWA <sup>1</sup>	(ppm)
Arsine	0.05
Diborane	0.1
$\text{ClF}_3$	0.1
Germane	0.2
Phosphine	0.3
<b>Fluorine (<math>\text{F}_2</math>)</b>	<b>1</b>
<b>HF</b>	<b>3</b>
Silane	5
$\text{NF}_3$	10
CO	25

Note1: TLV/TWA is defined as Threshold Limit Value/Time-Weighted Average. It is the maximum permitted workday exposure recommended by the ACGIH.

Table 1: TLVs (Threshold Limit Value) for common gas-phase, thin-film feedstocks

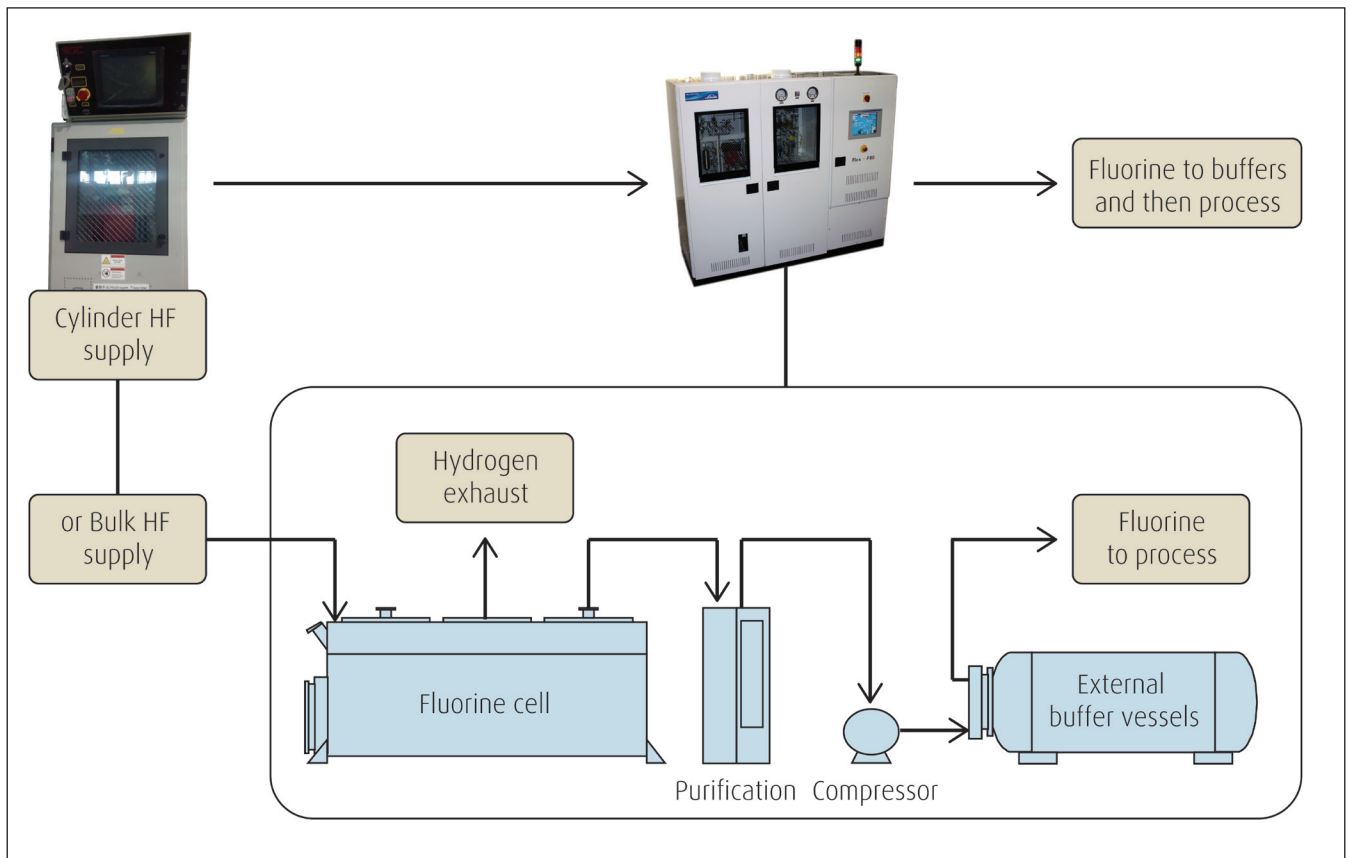


Figure 2:  
Process flow  
diagram for on-  
site generated  
fluorine

**Mitigation strategy: Material selection and passivation**

Although fluorine is highly reactive, many common metal constructions are compatible with fluorine at process temperatures. These include brass, copper, nickel, and many steel and nickel alloys, all of which form chemically inert, passivated metal fluoride layers when properly prepared.

Components for the generation, containment, and transport of fluorine should first be cleaned of all particles and residues – the same as for oxygen service – and certified leak-free. They are then exposed to a sub-atmospheric partial pressure of fluorine, often diluted in an inert gas.

Any organic residues are converted to gas-phase fluorides and exhausted to a scrubber, while the native oxide layers of the metal are replaced to form metal fluorides. By gradually raising the partial pressure to the maximum working pressure, the metal fluoride passivation layer is deepened, and the metal surfaces are rendered inert to further reaction with fluorine.

In addition, properly-sized piping and elimination of sharp bends are required to reduce gas velocities below the industry-recognized safe levels [Reference: Compressed Gas Association CGA publication 9-15;

European Industrial Gas Association EIGA document 140/10].

**Mitigation strategy: Containment**

Containment forms the second safety risk mitigation strategy. All super-atmospheric sources of fluorine are contained by either ventilated enclosures or sealed and sectioned annular piping.

Ventilated enclosures house all generation and compression equipment, purification and buffer vessels, and valve manifold boxes. Extraction rates are determined to maintain safe external conditions in the event of a rapid release of the limited inventory. Extracted air is treated by either a local or facility acid scrubber.

Toxic gas detectors specific to fluorine are used to monitor all extracted areas. Transport of fluorine within the facility is through double-layered piping. The fluorine flows in the center tube while the annular space is sectioned and pressurized with nitrogen.

A leak from the center tube can be detected as a pressure loss in the annular space, and fluorine is doubly contained by both the outer pipe and the nitrogen barrier. A leak detected by a toxic

gas monitor or by depressurization of the annular containment triggers suspension of fluorine generation and automated closure of fail-closed valves.

### Mitigation strategy: Design

On-site fluorine generation has been sized to meet the requirements of a number of thin-film chamber cleaning processes. Originally conceived as a replacement for high-pressure cylinders of  $F_2$  and  $ClF_3$  (chlorine trifluoride) used for cleaning low-pressure chemical vapor deposition (LP-CVD) semiconductor equipment, the smallest sized units have an annual production capacity of 1 ton / year. The equipment is designed in standard modules with form factors similar to gas cylinder cabinets.

Along with the availability of gas blenders with very low pressure-drop components, these units make for a direct replacement of 20 percent  $F_2$  / 80 percent nitrogen ( $N_2$ ) cylinder supplies. Almost all safety incidents in the semiconductor industry with fluorine are associated with high-pressure cylinder supplies, and in particular, the regulators used. Because a single generator operating at low pressure can replace more than 500 cylinders per year, the safety of the process has been greatly improved.

Maintaining a minimal inventory is integral to the design and safe usage of fluorine. Because the fluorine is generated on-site, there is no need to compress it to high pressures in order to transport it in containers. Instead, a pressure of 1.5 barg is sufficient to supply all gas conditioning and mass flow equipment of the cleaning process. And because fluorine is generated on-demand and proportionally to the current applied to the electrodes, the only vessels used are sized to buffer the generator against the periodic requirement for cleaning gas.

Modeling of randomized demand from multiple tools, sometimes numbering more than 100 for a single on-site plant, ensures that the buffer vessels are sized adequately for all realizable demand without being oversized. For example, a plant with a name-

plate capacity of greater than 100 tons / year has an instantaneous inventory of less than 50 kg, which is little more than four hours of supply for a large LCD fab; fluorine supplies for semiconductor process have inventories as low as 2 kg at any time. As well as being made safe, on-site generated fluorine for thin-film chamber cleaning applications must meet the very high industry standards for reliability. Design and operation are essential to achieving high uptime. Beyond proper material and component selection, moving parts are minimized in the system design, electrochemical duty is kept light, and preventative maintenance and monitoring use leading indicators to keep all performance parameters within controlled ranges.

The design of the on-site generation configuration uses  $n+1$  redundancy of key components and modularization of assemblies. Therefore, preventative maintenance and repairs can be performed quickly without compromising the ability to supply the process, and longer-term service can be accomplished off-site. In addition to on-site operators, most fluorine plants for thin-film chamber cleaning take advantage of remote monitoring. This allows 24 hours per day coverage and diagnostics by fluorine plant experts located on three continents.

The design for safety and reliability have been recognized and accredited by a number of design authorities and awarding bodies: certification to CE, ASME, Korean S-mark, and SEMI S2, and awards by Semiconductor International for Best Product 2009 and from International Solar Technology for Green Solar Manufacturing 2009.

With the advent of the high-volume manufacturing of LCD screens and thin-film photovoltaic modules, the demand for on-site generated fluorine has grown in scale. In these applications, fluorine is used as a chamber cleaning agent for plasma-enhanced chemical vapor deposition (PE-CVD) processes. Larger generators have been designed for supplying 100s of tons / year. And although the process design

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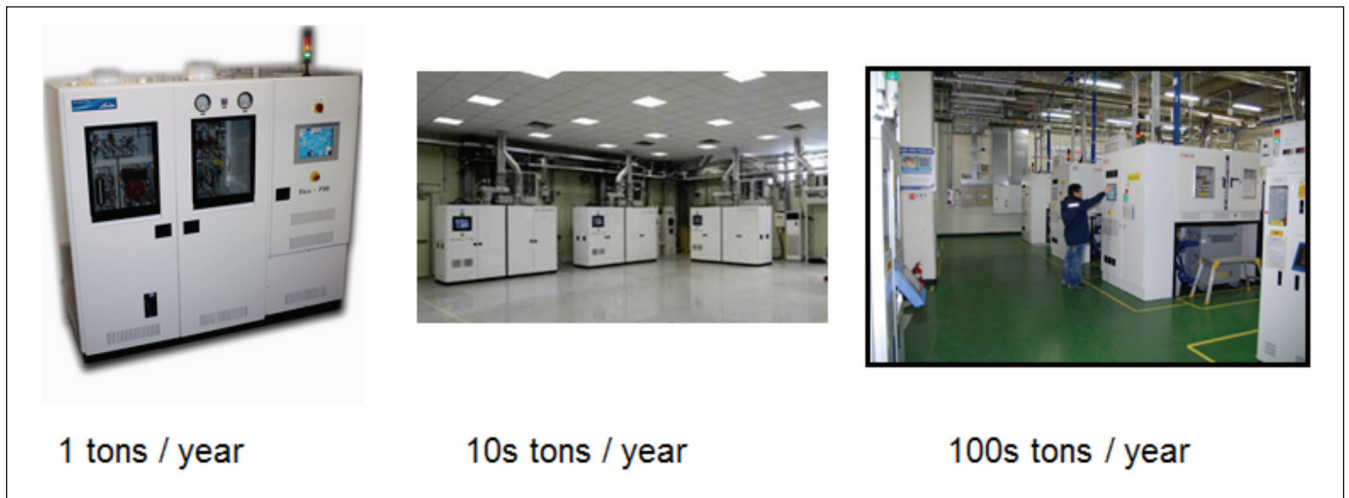


Figure 3: Three generations of on-site fluorine generators. Generators are available in different sizes and configurations to offer a wide range of capacity options.

remains the same, the form factor for these systems has grown to a separate on-site facility. This mirrors the track to other on-site supply schemes, such as those for nitrogen, oxygen, and hydrogen, from which manufacturers benefit as they scale their operations to achieve critical capacity.

The supply of on-site generated  $F_2$  differs in several areas from the use of  $SF_6$  or  $NF_3$  for cleaning thin-film equipment. On-site supply schemes require different project considerations when compared to packaged material supplies to ensure proper footprint, utilities availability, and expansion capability.

Planning for safety is integrated with the end user and community at an early stage, and additional activities are required for commissioning and operation. Likewise, permitting and licensing change, with the added benefit that the on-site chemical inventory is substantially reduced. Furthermore, risks to supply chains and pricing volatility are reduced.

### Summary

In the last 20 years, Linde has installed over 30 on-site fluorine generators, which are successfully operated in 11 countries. These continue to operate without a single safety incident, and provide supply delivery reliability much greater than 99 percent.

In Part II of this article series, we will discuss the fundamental chemical properties of fluorine that allow it to deliver significant process and cost of ownership benefits while at the same time eliminating the need for the majority of greenhouse gas usage in high-tech, thin-film manufacturing. Used in increasingly higher volumes, gases like  $NF_3$ ,  $SF_6$ , and  $C_2F_6$  have global warming potentials thousands of times greater than  $CO_2$  and are coming under stringent monitoring and reduction regulations as more aggressive measures are enacted to reverse trends in climate change.

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## On-Site Generated Fluorine: High-speed chamber cleaning with zero global warming potential

On-site generated fluorine enables faster chamber cleaning and eliminates the need for the largest use of restricted greenhouse gases in semiconductor manufacturing processes.

Dr. Paul Stockman, Head of Market Development at Linde Electronics, explains the chemical properties underlying the benefits.

IN PART 1 OF THIS ARTICLE [1], we described the safe and reliable on-demand production of fluorine as demonstrated by Linde's on-site fluorine generators, with an installed base of more than 30 systems over the last 20 years and more than 15 years serving electronics manufacturers. With production capacities of one to hundreds of tons per year, these systems first displaced cylinder sources of  $F_2$  and  $ClF_3$  used for chamber cleaning of semiconductor processes, and have subsequently become the preferred bulk supply of chamber cleaning agents for large LCD and thin-film photovoltaic manufacturing. In Part II, we discuss the fundamental chemical properties of fluorine that allow it to deliver significant process and cost of ownership benefits, while at the same time eliminating the need for the majority of greenhouse gas (GHG) usage in high-tech manufacturing.

### Chamber cleaning requirement

Chemical vapor deposition (CVD) processes used in high-tech thin film manufacturing require periodic cleaning to remove particles and films from the

surfaces of the vacuum chamber and process equipment. The frequency of the cleaning can be as short as once per deposition cycle, or may range up to once per several days, depending upon the thickness of the film deposited and the sensitivity of the devices being made. Without cleaning, these films and particles lead to defects that render semiconductor chips inoperable, displays with dark pixels, and solar modules with degraded efficiencies.

Most high throughput CVD processes employ automated, on-line cleaning with gas-phase chemicals as a time-saving alternative to off-line manual and wet processes. These gases must not only react with compounds in the deleterious films and particles, but also must be non-reactive towards the chamber materials of construction. In order to maximize the availability of the costly CVD equipment, chamber cleaning processes must be quick. And increasingly, device manufacturers are looking for processes that have low environmental impact and long-term sustainability. Most importantly, the cleaning processes must be very low cost per process cycle: it's cleaning, after all.

## F-gases and activation

Fluorine-containing gases, or F-gases, meet all of the technical and cost requirements for chamber cleaning agents. The gases are activated to release the fluorine atoms as neutral radicals, which subsequently react

with residual thin-films to form a gas-phase waste stream and are removed through the vacuum exhaust system of the chamber. While very reactive towards the thin-film compounds, fluorine radicals are inert towards most of the metals and ceramics used in CVD equipment, provided that moisture and oxygen are excluded.

Historically, the electronics industry has used fluorocarbons ( $C_xF_y$ ): sulfur hexafluoride ( $SF_6$ ), and nitrogen trifluoride ( $NF_3$ ) as feedstocks to supply the fluorine radicals. These gases are easy to compress and transport in cylinders, and the cost to supply has been reduced through higher-volume manufacturing and packaging. However, these gases have certain process inefficiencies inherent to the high bond strengths and side reactions associated with the carbon / sulfur / nitrogen carrier atoms. These gases have also been the target of environmental scrutiny and regulation because they are all very strong greenhouse gases with global warming potentials thousands of times that of  $CO_2$ . As a cost-effective alternative, fluorine ( $F_2$ ) has zero global warming potential (GWP) and none of the process inefficiencies of the earlier chamber cleaning agents.

Three methods can be used to activate the F-gases to release fluorine radicals [Figure 1]. In low-pressure CVD (LPCVD) process equipment operated at very high temperature, greater than  $700^\circ C$ , the thermal

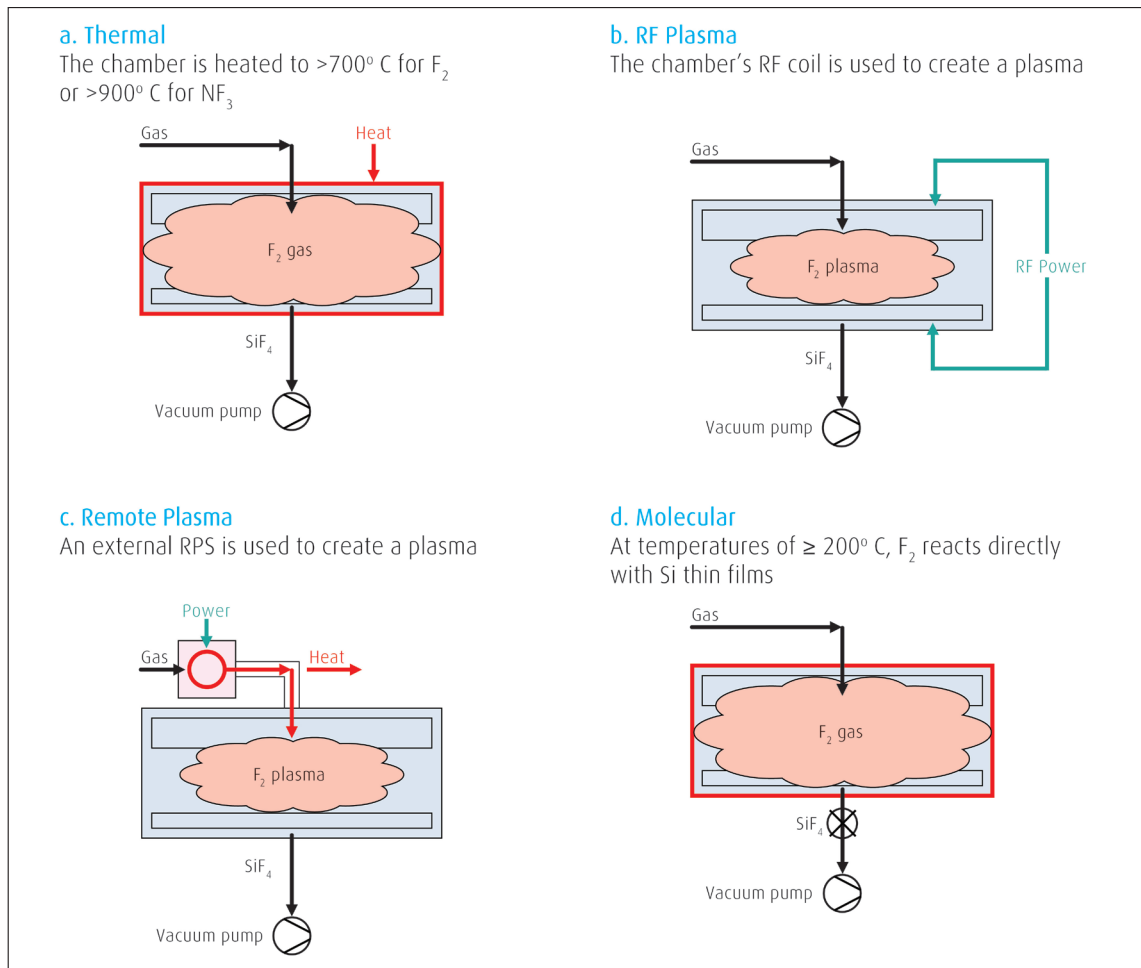


Figure 1: Activation methods for CVD chamber cleaning





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energy from the chamber walls is sufficient to break the molecular bonds and release fluorine radicals. In plasma-enhanced CVD (PECVD) equipment, process temperatures are much lower, and too much time would be spent to heat and then cool the chamber for cleaning. Instead, the internal RF coil used to activate the plasma of the thin film reactants is also used to activate the F-gas cleaning agent. The cleaning rate is limited by the amount of energy that can be supplied by the RF power source.

With the advent of larger, more expensive 300 mm PECVD equipment, external remote plasma sources (RPS) were introduced in order to increase the energy available for cleaning gas activation, thereby decreasing the cleaning time. Most current generation PECVD tools use this method to increase the tool availability. Importantly, argon is not required to support the plasma in the RF or RPS methods. Finally, a fourth method using a low temperature direct reaction between molecular F<sub>2</sub> and the silicon thin film has been demonstrated as a very fast alternative method for this application. [2]

**Thermodynamics and kinetics: Theory**

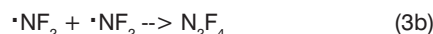
Both the thermodynamics – or chemical energy – and kinetics – or chemical pathways – of cleaning gas activation need to be considered to understand and exploit the significant process advantages available when using F<sub>2</sub> vs. other F-gas alternatives. After a short look at this fundamental science, we will present process data from a variety of tools and applications that demonstrate these advantages.

As the most electronegative atom in the periodic table, fluorine forms strong bonds with most other atoms, including some stable compounds with rare gases. It is not surprising then that C<sub>x</sub>F<sub>y</sub>, SF<sub>6</sub>, and NF<sub>3</sub> all have very high bond energies – the amount of energy required to release fluorine radicals. In contrast, fluorine forms a very weak bond with itself, and therefore F<sub>2</sub> requires very little energy for activation. Table 1 shows the energy required to remove individual fluorine radicals from a given F-gas and summarizes the average energy of activation. In the subsequent examples, we will see how this translates into much higher cleaning rates achievable with F<sub>2</sub>.

Once the fluorine radicals are created through activation, chemical simplicity maximizes the amount of fluorine radicals that are available for cleaning from F<sub>2</sub>. There is only one chemical



pathway (1) that can be followed, and recombination in the gas-phase to reform F<sub>2</sub> is kinetically forbidden. Therefore, almost all of the fluorine radicals created from F<sub>2</sub> go on to react with the thin films and particles targeted for cleaning. With the addition of different atoms, there is more than one available pathway during activation. For example, with NF<sub>3</sub> and RF activation, at low



	F <sub>2</sub>		NF <sub>3</sub>		SF <sub>6</sub>	
Bond energies	F---F	159 kJ/mol	F <sub>2</sub> N---F	248 kJ/mol	F <sub>5</sub> S---F	387 kJ/mol
			FN---F	278 kJ/mol	F <sub>4</sub> S---F	229 kJ/mol
			N---F	316 kJ/mol		
Activation energy for each F atom produced	F from F <sub>2</sub>	80 kJ/mol	F from NF <sub>3</sub>	281 kJ/mol	F from SF <sub>6</sub>	308 kJ/mol

Table 1: Bond strengths and activation energy of CVD chamber cleaning gases

pressures, the desired pathway (3a) dominates. However, as the flow of  $NF_3$  and the RF power increase, recombination of the intermediates (3b) competes, with a result that only approximately 50 percent of the fluorine atoms become effective cleaning radicals [3].

With  $SF_6$ , the effect is even more pronounced, and oxygen is added to prevent the deposition of sulfur during the cleaning.



The effective net reaction (4) means that only 33 percent of fluorine atoms are actually used.

### Thermodynamics and kinetics: Results

Now we take a look at the process effects of the thermodynamics and kinetics on commercial PECVD tools for Gen 5 LCD processes from AKT/AMAT, Oerlikon, and Ulvac. In each case, a silicon thin film has been deposited on the chamber walls at an operating temperature of 200°C.

The cleaning gas flow has been normalized to atomic  $F \cdot$  in units of standard liter per minute (slm). The endpoint for the cleaning was determined by OEM recommended methods. The cleaning rates have been normalized to the OEM recommended method, which is set at 1.

In Figure 2 [2] and Figure 3, RF activation of  $F_2$  vs.  $SF_6$  and  $NF_3$  is compared, and the RF power used is noted in the figures. The results confirm the kinetics limitation on efficiency: 33 percent for  $SF_6$  and 50 percent for  $NF_3$  vs.  $F_2$ . Furthermore, for the same cleaning rates,  $F_2$  consumes one-third of the electrical power for activation.

And finally, for the same equipment set,  $F_2$  can achieve a much faster cleaning rate: 5x vs.  $SF_6$  and 3x vs.  $NF_3$ . This is due ultimately to the limitations of the power required for activation. Similar results have been published by others on 300 mm semiconductor tools [4].

Results in Figure 4 from a similar experiment using a tool with an RPS [5] demonstrate the improved utilization of  $NF_3$  with this method of activation. Because the RPS completely decomposes the cleaning gas, all the fluorine is converted to fluorine radicals and the cleaning rates are the same for  $F_2$  and  $NF_3$  for the same amount of atomic  $F \cdot$  flow.

However, because the  $F_2$  bonds are so much weaker than those from  $NF_3$ , the RPS can convert much more  $F_2$  into  $F \cdot$  radicals and the achievable cleaning rate for  $F_2$  is 3x to 4x that of  $NF_3$ . And for the same cleaning rate,  $F_2$  cleaning requires 50 percent of the RPS electrical power required for  $NF_3$ . Finally, because there is no carrier atom in  $F_2$ , 20 percent less mass is used to achieve the same clean vs.  $NF_3$ .

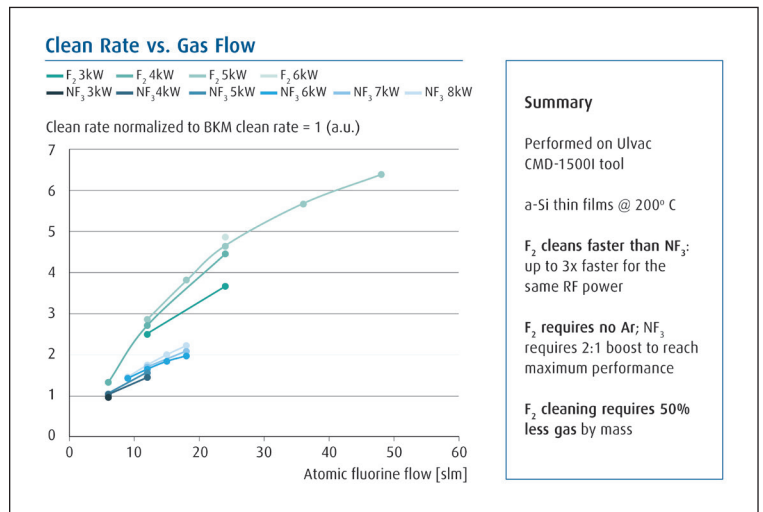


Figure 2: RF Plasma cleaning on an Ulvac tool:  $F_2$  vs.  $NF_3$

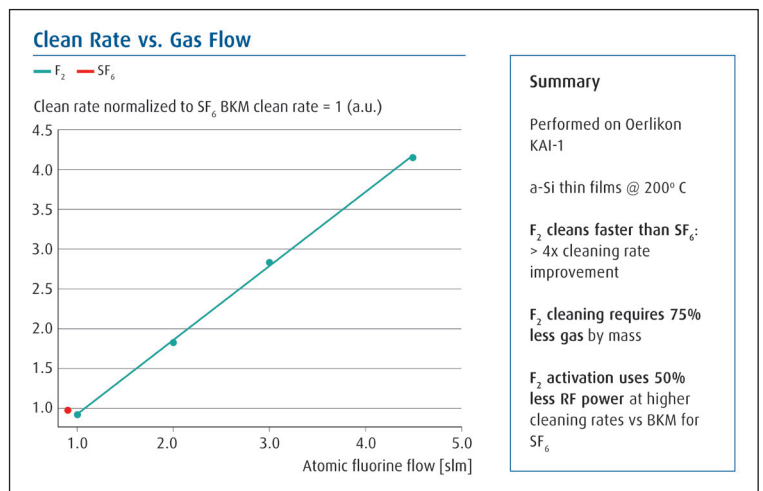


Figure 3: RF plasma cleaning on an Oerlikon tool:  $F_2$  vs.  $SF_6$

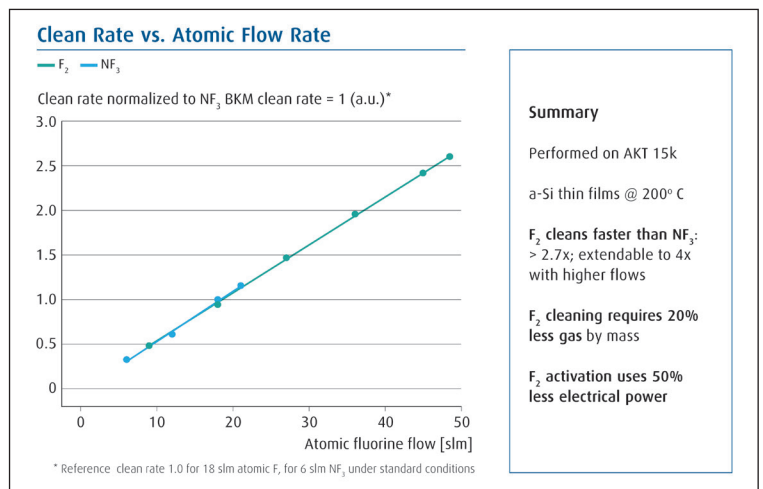


Figure 4: RF plasma cleaning on an AKT tool:  $F_2$  vs.  $NF_3$

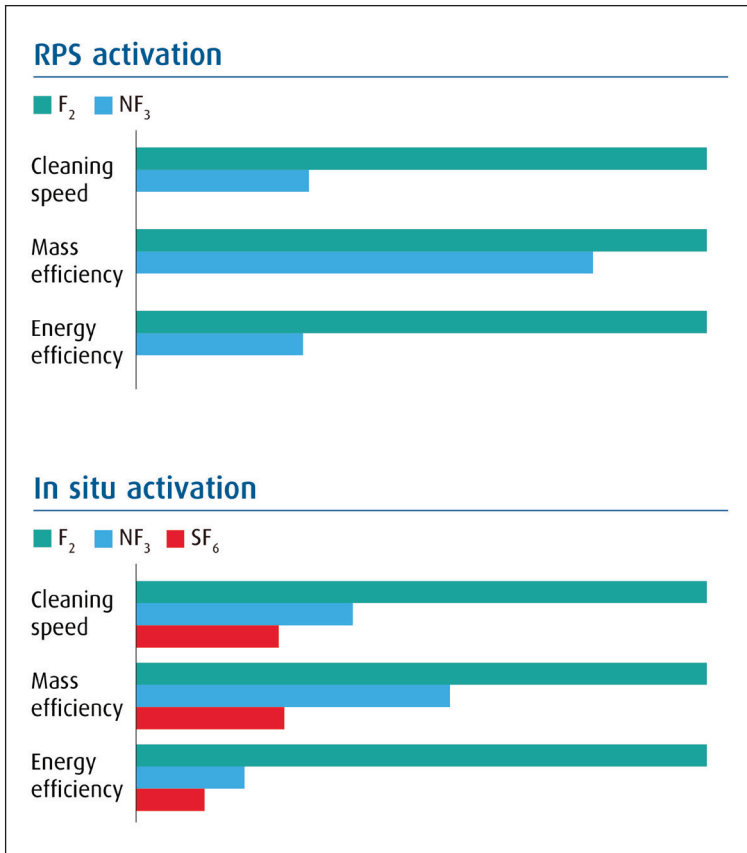


Figure 5: Summary of PECVD chamber cleaning performances

Figure 5 summarizes the  $F_2$  process benefits vs.  $SF_6$  and  $NF_3$  for speed, mass efficiency, and energy efficiency demonstrated for chamber cleaning. Faster cleaning, less gas used, and lower energy consumption are achieved across all of the tested PECVD tools. While the other chamber cleaning methods discussed above rely on first converting F-gases to F radicals, there exists an alternate cleaning method unique to  $F_2$  for silicon films. The responsible kinetic mechanism is a direct reaction between  $F_2$  and the silicon surface [6]. As seen in Figure 6, the cleaning rate is directly related to the amount and pressure of  $F_2$  available. This method has been further demonstrated to be achievable under zero flow conditions, indicating a very fast and cost-effective clean [3].

**On-site fluorine: The zero global warming potential choice**

Beyond the significant process benefits demonstrated by using  $F_2$  as a chamber cleaning agent, growing adoption of  $F_2$  also alleviates serious problems associated with the use of GHGs like  $C_xF_y$ ,  $SF_6$ , and  $NF_3$ . Unlike GHGs,  $F_2$  does not absorb UV radiation and convert it to heat energy, and therefore it does not have any global warming potential (GWP) or contribute to global warming. Table 2 (see page 12) illustrates the very large GWPs associated with other chamber cleaning gases.

In 1990,  $C_xF_y$  and  $SF_6$  gases were recognized for their potential to damage the environment and were included in the Kyoto Protocol for the reduction of GHGs. Large-scale adoption of  $NF_3$  for chamber cleaning began just after this time. Scripps Institute scientists, tasked by the US government since the 1970s to collect atmospheric samples for monitoring of ozone-destroying compounds, analyzed their repository and found that  $NF_3$  has been growing at a semi-exponential and unabated rate since industrial use began in the 1990s [7]. They showed that more than 10 percent of  $NF_3$  produced ultimately escapes into the atmosphere. Recently, several national and local environmental authorities have moved to monitor the use of  $NF_3$ . The US Environmental Protection Agency has included  $NF_3$  and other GHGs commonly used in the electronics industry as part of its reporting rule. Manufacturers are required to report not only the amount of individual GHGs used, but also to measure the gases at key steps in their processes.

While not yet regulated by means of a carbon equivalent tax, the cost of compliance is estimated at over \$1 million (USD) for larger fabrication facilities [8]. Because cleaning gases constitute approximately two-thirds of the GHGs used in a typical semiconductor fab, converting PECVD chamber cleaning to fluorine will allow some mid-tier manufacturers to decrease their total GHG usage below the reporting threshold, while the largest manufacturers will be able to significantly reduce their compliance burden.

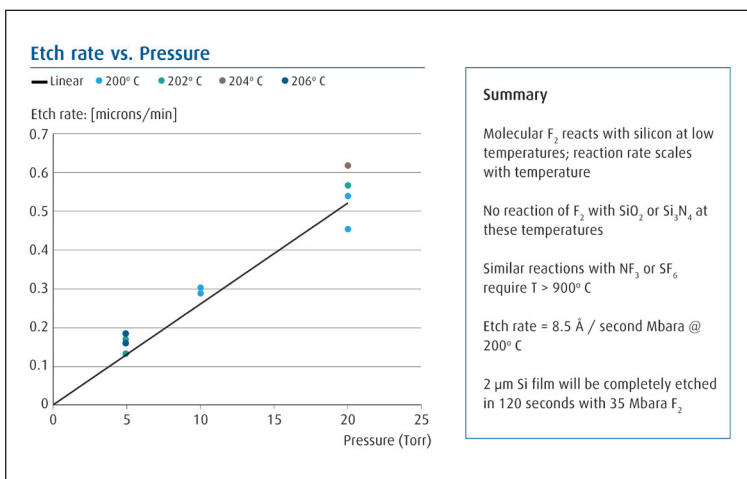


Figure 6: Molecular cleaning with  $F_2$

Clean Gas	Atmospheric Lifetime	Global Warming Potential
CF <sub>4</sub>	50,000 years	6,500 GWP <sub>100</sub>
C <sub>2</sub> F <sub>6</sub>	10,000 years	9,200 GWP <sub>100</sub>
C <sub>3</sub> F <sub>8</sub>	2,600 years	7,000 GWP <sub>100</sub>
SF <sub>6</sub>	3,200 years	23,900 GWP <sub>100</sub>
NF <sub>3</sub>	740 years	17,200 GWP <sub>100</sub>
F <sub>2</sub>	0 years	0 GWP <sub>100</sub>


Table 2: Global warming potentials of CVD chamber cleaning gases

**Summary**

Manufacturers in the semiconductor, display, and photovoltaic industries have safely and reliably chosen on-site F<sub>2</sub> for their CVD chamber cleaning requirements. Initially adopted for its cost and process enhancement benefits, F<sub>2</sub> is now proving to be an easy choice for manufacturers who also want an environmentally sustainable alternative.

For the past 20 years, Linde has been the leader in providing on-site fluorine generation for the electronics industry and other markets. With over 30 installations, Linde continues to support its customers' choice for faster, more efficient cleaning processes with zero global warming potential. Linde partners with manufacturers and OEMs for the extension of these benefits to additional applications.

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DR. PAUL STOCKMAN joined Linde in 1996. He currently is Head of Market Development, Linde Electronics, where he guides Linde's strategy to anticipate the needs of its customers in the semiconductor, display, solar and LED markets. During his career with Linde, Dr. Stockman has held roles in electronic materials product, purification and analytical development; equipment development; as well as Technology and Commercialisation Manager for Linde's on-site fluorine equipment. Dr. Stockman has been granted 5 U.S. patents and holds a Ph.D. in Chemical Physics from the California Institute of Technology.

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