

Fluorine Use in the Electronics Industry

By Dr. Paul Stockman

Fluorine (F₂) is used in the high-tech thin film industries of semiconductor, display, and photovoltaic manufacturing. Chemical vapor deposition (CVD) processes in this type of manufacturing require periodic cleaning — as often as once per deposition cycle or up to once per several days, depending on the thickness of the film deposited and the sensitivity of the devices being made — to remove particles and films from the surfaces of the vacuum chamber and process equipment.

Cleaning gases comprise two-thirds of the GHGs (greenhouse gases) used in a typical semiconductor fab. Converting PECVD (plasma-enhanced chemical vapor deposition) chamber cleaning to fluorine enables some mid-tier manufacturers to decrease their GHG below the reporting threshold and large manufacturers can significantly reduce their compliance burden.

Cost of compliance at large fabs can be over \$1 million. Manufacturers have to report the amount of GHGs used and measure the gases at key steps in their processes. Fluorine is an alternative to greenhouse gases — which also have process inefficiencies — such as CF₄ (tetrafluoromethane), SF₆ (sulfur hexafluoride), NF₃ (nitrogen trifluoride), and C₂F₆ (hexafluoroethane) for CVD cleaning. Unlike GHGs, fluorine does not

absorb infrared radiation and convert it to heat energy, and therefore has zero global warming potential (GWP) or contribute to global warming.

For the largest use applications, fluorine is a direct replacement for NF₃ without the need for further process development. On the same equipment, fluorine can clean three to five times faster. Compared with NF₃, fluorine cleaning has a much lower thermal effect on the chamber, meaning the overall cleaning cycle is significantly shorter.

Fluorine is the most electronegative element from the periodic table so the risks associated with its reactivity and toxicity must be mitigated, like for any chemical. For small volumes, cylinders are available. It can be transported in large volumes as a cryogenic liquid or compressed gas, but it is safer to produce in on-demand volumes on-site at low or atmospheric pressure, as its reactivity is directly related to its pressure. Double containment and material selection are the keys to design for safety and reliability.

Incorporating fluorine has different project considerations for an on-site supply scheme compared to packaged material supplies to ensure proper footprint, available utilities, and expansion capability. With on-site production, chemical inventory, safety risks, and pricing volatility



Linde Generation-F™ on-site fluorine generators

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are substantially reduced and supply and reliability are increased as process demands scale.

Linde Generation-F™ on-site fluorine generators range in output production capacity from one ton a year to hundreds of tons a year. There have been over 30 Linde installations of fluorine generators in the last 20 years and they have operated without a single safety incident.

Compared to greenhouse gas producing alternatives such as NF₃ and SF₆, fluorine has been measured to do faster cleaning, use less gas, and consume lower energy across all of the tested PECVD tools, and is becoming more widely adopted in the electronics industry. SGR

About the Author

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

Figure 1

Source: Linde Electronics