

Fluorinated Substitutes: The Lesser Evils?

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Last month, we discussed the [global warming effect resulting from hydrofluorocarbons \(HFCs\), perfluorocarbons \(PFCs\), and sulfur hexafluoride \(SF₆\)](#), which were introduced to replace the ozone-depleting, global-warming chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Most greenhouse gas (GHG) emissions are produced as by-products of industrial processes, as shown in Table 1.

Table 1 U.S. greenhouse gas emissions (MMTCE)

Numbers in italics represent emissions from industrial processes, numbers in parentheses represent emissions from the semiconductor industry

Gas/Source	1990	1995	2000	2005	2006	2007	2008
CO₂	5,100.8	5,427.3	5,977.2	6,108.4	6,017.2	6,120.2	5,921.2
	<i>191.5</i>	<i>192.6</i>	<i>187.7</i>	<i>167.0</i>	<i>171.5</i>	<i>174.0</i>	<i>162.1</i>
	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)
CH₄	613.4	613.2	586.0	553.2	568.2	569.2	567.6
	<i>1.9</i>	<i>2.1</i>	<i>2.2</i>	<i>1.8</i>	<i>1.7</i>	<i>1.7</i>	<i>1.6</i>
	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)
N₂O	322.3	342.5	345.5	328.3	329.5	327.7	318.2
	<i>34.7</i>	<i>38.6</i>	<i>26.3</i>	<i>22.6</i>	<i>21.5</i>	<i>24.2</i>	<i>21.1</i>
	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)	(<i>NA</i>)
HFCs	36.9	62.2	103.2	119.3	121.8	127.4	126.9
	<i>36.9</i>	<i>62.2</i>	<i>103.2</i>	<i>119.3</i>	<i>121.8</i>	<i>127.4</i>	<i>126.9</i>
	(<i>0.2</i>)	(<i>0.3</i>)	(<i>0.3</i>)	(<i>0.2</i>)	(<i>0.3</i>)	(<i>0.3</i>)	(<i>0.3</i>)
PFCs	20.8	15.6	13.5	6.2	6.0	7.5	6.7
	<i>20.8</i>	<i>15.6</i>	<i>13.5</i>	<i>6.2</i>	<i>6.0</i>	<i>7.5</i>	<i>6.7</i>
	(<i>2.2</i>)	(<i>3.8</i>)	(<i>4.9</i>)	(<i>3.2</i>)	(<i>3.5</i>)	(<i>3.6</i>)	(<i>4.0</i>)
SF₆	32.6	27.9	19.1	17.8	17.0	16.1	16.1
	<i>32.6</i>	<i>27.9</i>	<i>19.1</i>	<i>17.8</i>	<i>17.0</i>	<i>16.1</i>	<i>16.1</i>
	(<i>0.5</i>)	(<i>0.9</i>)	(<i>1.1</i>)	(<i>1.0</i>)	(<i>1.0</i>)	(<i>0.8</i>)	(<i>1.1</i>)
Total*	6,126.8	6,488.7	7,044.5	7,133.2	7,059.7	7,168.1	6,956.7
	<i>318.3</i> (<i>2.9</i>)	<i>339.1</i> (<i>4.9</i>)	<i>351.9</i> (<i>6.2</i>)	<i>334.7</i> (<i>4.4</i>)	<i>339.7</i> (<i>4.7</i>)	<i>350.9</i> (<i>4.7</i>)	<i>334.5</i> (<i>5.4</i>)

Source: United States Environmental Protection Agency, 2010

*Note: Totals may not sum due to independent rounding.

In the electronics (semiconductor, thin-film transistor display, and photovoltaics) industries, manufacturers perform plasma etching and CVD chamber cleaning using PFCs (e.g., CF₄, C₂F₆, C₃F₈), nitrogen trifluoride (NF₃), HFC-23 (CHF₃), and SF₆, whose atmospheric lifetimes and global warming potentials (GWPs) are shown in Table 2.

Table 2 Atmospheric lifetimes and global working potentials of select greenhouse gases used in the electronics industry

Gas		Atmospheric Lifetime (years)	GWP ₁₀₀	Semiconductor/Display/PV Process	
				CVD Chamber Cleaning	Plasma Etching
Carbon dioxide	CO ₂	Variable	1	NA	NA
Methane	CH ₄	12	25	NA	NA
Nitrous oxide	N ₂ O	114	298	X	
Tetrafluoromethane	CF ₄	50,000	7390		X
Octafluoropropane	C ₃ F ₈	2600	8,830	X	
Octofluorocyclobutane	c-C ₄ F ₈	3,200	10,300	X	X
Trifluoromethane (HFC-23)	CHF ₃	270	11,700		X
Hexafluoromethane	C ₂ F ₆	10,000	12,200	X	X
Nitrogen Trifluoride	NF ₃	740	17,200	X	X
Sulfur hexafluoride	SF ₆	3200	22,800		X

Source: Intergovernmental Panel on Climate Change, United States Environmental Protection Agency

Most HFC, PFC, and SF₆ emissions in electronics production are due to inefficient utilization of the fluorinated precursors during etching or cleaning. Some of the fluorinated compounds used in the production process can be converted into by-product CF₄, C₂F₆, CHF₃, and C₃F₈. Some CF₄ can form as a by-product of etching or cleaning carbon-containing low-k dielectric materials.

Electronics manufacturers also use fluorinated compounds as heat transfer fluids for temperature control during certain processes. They are liquids at room temperature and have appreciable vapor pressures. Evaporative losses occur during cooling of process equipment, testing of packaged semiconductor devices, and vapor-phase-reflow soldering of electronic components to circuit boards. These losses all contribute to GHG emissions.¹

While N₂O is not a PFC, it is a GHG with high GWP. It is used in oxynitride deposition processes and its use and resulting emissions must be monitored. In 1999, the World Semiconductor Council (WSC) set a target of reducing emissions 10% below the 1995 baseline by 2010. Replacing high GWP gases is a high priority but each substitute must be more environmentally-benign than the gas it replaces. Ideally, these substitutes do not have high GWPs (or are eliminated during manufacturing if they do) and do not form by-products with

high GWPs, such as CF₄ and CHF₃. Factors taken into consideration include etch rate, etch profile, etch selectivity, and control of critical dimension. Substitutes are deemed unsuitable if the cleaning or etch times are increased substantially, or if new health or safety hazards are introduced.

According to EPA's latest U.S. Greenhouse Gas Inventory Report, PFC, HFC, and SF₆ emissions from U.S. semiconductor manufacturing totaled 5.4 MMTCE in 2008 (Table 3), compared to 2.9 MMTCE in 1990, 4.9 MMTCE in 1995, and 7.2 MMTCE when emissions peaked in 1999. Combined emissions from all industrial processes in 2008 totaled 334.5 MMTCE (5% of total U.S. GHG emissions), with 149.7 MMTCE from fluorinated gases (Table 1).² It is worth noting that the U.S. semiconductor industry contributes to 59.7% of total PFC emissions in 2008, compared to 48% in 2007, 58.3% in 2006, 51.6% in 2005, 36.3% in 2000, 24.4% in 1995, and 10.6% in 1990 (all PFC emissions in the U.S. are by-products of industrial processes).

Table 3 PFC, HFC, and SF₆ Emissions from Semiconductor Manufacturing (MMTCE)

Gas/Source	1990	1995	2000	2005	2006	2007	2008
CF ₄	0.7	1.3	1.8	1.1	1.2	1.3	1.3
C ₂ F ₆	1.5	2.5	3.0	2.0	2.2	2.3	2.6
C ₃ F ₈	0.0	0.0	0.1	0.0	0.0	0.0	0.0
C ₄ F ₈	0.0	0.0	0.0	0.1	0.1	0.1	0.1
HFC-23	0.2	0.3	0.3	0.2	0.3	0.3	0.3
SF ₆	0.5	0.9	1.1	1.0	1.0	0.8	1.1
NF ₃ *	0.0	0.1	0.2	0.4	0.7	0.5	0.4
Total**	2.9	4.9	6.2	4.4	4.7	4.7	5.4

Source: United States Environmental Protection Agency, 2010

* NF₃ emissions are presented for informational purposes, using a GWP of 17,200, and are not included in totals.

**Note: Totals may not sum due to independent rounding.

Dry cleaning and etch processes rely on surface chemistries that use reactive gases. Critical players in these reactions are the free radicals generated in the plasma to react with the materials to be etched or removed. Products of the etching reaction should have sufficiently high vapor pressures at the substrate operating temperature so they can rapidly desorb and exit the process chamber. Gaseous halogen compounds are often used, with fluoride and chloride species being preferred because they are less corrosive and easier to handle than the bromides and iodides.³ Most dielectric etch processes use fluorine chemistry with heavy ion bombardment and the damaging mechanism is employed to achieve anisotropic etch profile. Fluorine is required to etch the desired features into the dielectric material and carbon is required to passivate newly-etched surfaces by forming C_xF_y polymers that are deposited to hold off etching. The boundary between net etching and deposition is a function of the F:C ratio in the discharge because

plasmas rich in fluorine favor etching over deposition and those rich in carbon favor deposition over etching.^{3,4} Most commonly used gases are fluorocarbons (also known as carbon fluorides) such as CF₄, CHF₃, C₂F₆, and C₃F₈ while some oxide etch systems use SF₆ as the fluorine source gas. In a plasma, these gases dissociate and generate highly-reactive, free fluorine radicals.

The emergence and rapid growth of chip-to-chip interconnects (3D technology) is adding a new application — through-silicon via etch using SF₆ — to the list of global-warming culprits. This latest technology will add further strain on the semiconductor industry's ability to meet the WSC GHG-reduction goal.⁵

There are currently no alternatives to the use of fluorinated gases for plasma etch and CVD chamber cleaning in semiconductor manufacturing. To reduce the impact on the environment, industry leaders have adopted fluorinated substitutes with lower GWPs, optimized processes to more efficiently use fluorinated GHGs to reduce emissions, and implemented abatement or recycling technology to properly contain emitted GHGs.

It is important to remember that the non-ozone-depleting fluorinated substitutes are still greenhouse gases. Fluorinated compounds are very potent GHGs because of their long atmospheric lifetimes and high GWPs that are several hundred to several tens of thousands of times that of CO₂.

Due to its extremely high GWP and widespread usage, SF₆ was one of the first GHGs examined. Various substitutes have been evaluated to replace SF₆ as a CVD cleaning gas: C₂F₆/O₂, CF₂OF/O₂, F₃NO/Ar, COF₂/O₂, NF₃/Ar, F₂/Ar, and F₂/Ar/N₂. Efforts to replace C₂F₆ include switching to c-C₄F₈ and c-C₄F₈O, C₃F₈, COF₂, ClF₃, or NF₃. At some facilities and in the growing solar sector, on-site F₂ generators have been used successfully to replace NF₃, which was originally selected due to its cleaning efficiency and reduced climate impact compared to C₂F₆.

Regardless of their global warming potential, the manufacture and use of substitute gases that provide fluorine involve highly-reactive source gases that are volatile or corrosive. Production, delivery, and storage of low/zero-GWP gases such as F₂, COF₂, and ClF₃ involve high risks to safety, high costs of implementation, and uncertain environmental impact. Watch out for more coverage on these subjects in future issues of the *G&I* newsletter and magazine.

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¹ "Electronics Industry Emissions," *IPCC Guidelines for National Greenhouse Gas Inventories*, Intergovernmental Panel on Climate Change (2006)

² *Inventory Of U.S. Greenhouse Gas Emissions And Sinks: 1990 – 2008*, U.S. Environmental Protection Agency, EPA 430-R-10-006 (Released April 15, 2010)

³ S.K. Ghandi, "Etching and Cleaning," *VLSI Fabrication Principles: Silicon and Gallium Arsenide*, 2nd Ed., p. 630, Wiley Interscience (1994)

⁴ U.S. Climate Change Technology Program — Technology Options for the Near and Long Term, p. 4.3-4 (August 2005)

⁵ "Environment, Safety, and Health," *International Technology Roadmap for Semiconductors*, 2009 Edition