

Reduction of Perfluorocompound (PFC) Emissions: 2005 State-ofthe-Technology Report

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Reduction of Perfluorocompound (PFC) Emissions: 2005 State-of-the-Technology Report Technology Transfer #05104693A-ENG International SEMATECH Manufacturing Initiative December 2, 2005

Abstract: This report from the ESHI002M project reviews the current state perfluorocompound (PFC) technology development and implementation and describes the semiconductor industry's efforts to reduce PFC emissions. It documents pre-competitive information about potential PFC emission reduction processes and technology obtained from a survey of members of the International SEMATECH Manufacturing Initiative (ISMI); the Semiconductor Industry Association (SIA); the World Semiconductor Council (WSC); and chemical, tool, and abatement device suppliers. The appendix includes details about process optimizations, alternative processes, and abatement technologies.

- **Keywords:** Emissions Reduction, Perfluorocompounds, Pollution Control Equipment, Global Climate Change, Chamber Cleaning, Process Optimization
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1 EXECUTIVE SUMMARY

This report describes the semiconductor industry's efforts to reduce perfluorocompound (PFC) emissions, reviewing the current state of PFC technology development and implementation. It documents pre-competitive information about potential PFC emission reduction processes and technology obtained through a survey of members of the International SEMATECH Manufacturing Initiative (ISMI); the Semiconductor Industry Association (SIA); the World Semiconductor Council (WSC); and chemical, tool, and abatement device suppliers. The appendix includes details about process optimizations, alternative processes, and abatement technologies.

The industry is steadily decommissioning $\leq 150 \text{ mm}$ fabs, eliminating them as a source of PFC emissions. For the majority of operating $\leq 150 \text{ mm}$ fabs, process optimization and drop-in alternative chemistries for chemical vapor deposition (CVD) cleans may be the only alternatives for reducing emissions, although a few $\leq 150 \text{ mm}$ fabs have installed abatement on certain CVD processes. The 200 mm fabs can be divided into two distinct categories: older fabs with an installed base of CVD tools using perfluorocarbon clean chemistries and advanced fabs with lower emission NF₃-based cleans. In older 200 mm fabs, process optimization, installation of endpoint detection, installation of remote NF₃ cleans, and use of alternative clean chemistries are the most prevalent means of reducing emissions. Abatement is also being employed in some older 200 mm fabs. The industry and its suppliers have integrated low emission CVD tools into advanced 200 mm fabs. Several companies report using abatement technologies to reduce etch emissions in their advanced 200 mm and 300 mm fabs, and one company is using a central end-of-pipe (EOP) plasma unit to abate CVD emissions from an advanced 200 mm fabs. Capture/recovery may be appropriate for specialized high volume PFC applications.

The industry has undergone significant changes that impact PFC emissions. These changes include development and implementation of new chamber clean processes and chemistries, increased use of plasma etching and adoption of new etch gases, development of new materials and processes, and the use of larger wafers to manufacture advanced semiconductor devices. The change with the greatest impact on PFC emissions over time is increasing wafer size and the corresponding advanced processing technologies. As advanced 200 mm and 300 mm wafer fabs began ramping in 2001–2004, the normalized rate of emissions (PFC emitted/cm²) decreased, most likely due to the use of NF₃-based chamber clean processes. Based on the changes brought about by shifting wafer sizes and the projected acceleration in the transition from old technology to new, there is strong reason to believe the normalized rate of PFC emissions will continue to decline through 2010:

- The world semiconductor industry has demonstrated significant commitment to reducing PFC emissions.
- The U.S. semiconductor industry achieved the 10% reduction goal in 2003 and surpassed the goal in 2004, despite a significant increase in wafer demand over time.
- If the current normalized PFC emissions trend continues and wafer demand projections are accurate, the world-wide industry will achieve the 2010 goal; however, these trends and projections largely depend on the ramping up of lower emitting advanced 200 mm and 300 mm fabs and a decrease in the emissions from older, higher emitting fabs.

2 INTRODUCTION

As required by the SIA's memorandum of understanding with the Environmental Protection Agency (EPA), this report describes the semiconductor industry's efforts to reduce PFC emissions. It describes the current state of PFC technology development and the way the industry is implementing that technology. It reviews the impact of industry changes on historical and projected future emissions and SIA progress towards reducing PFC emissions. Finally, it projects future WSC emissions through 2010. This report is a follow-up to *Current State of Technology: Perfluorocompound (PFC) Emissions Reduction* [1], published in 1998.

3 BACKGROUND

It has been reported that PFCs have been identified as the most potent greenhouse gases measured due to their strong infrared absorption capacity [2]. PFCs are used in semiconductor manufacturing for plasma cleaning of CVD chambers and for plasma etching. Examples include tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), octofluoropropane (C₃F₈), octofluorocyclobutane (c-C₄F₈), nitrogen trifluoride (NF₃), sulfur hexafluoride (SF₆), and hydrofluorcarbons (HFCs) such as trifluoromethane (CHF₃). It has been reported that PFCs and the HFCs are referred to collectively by the industry as PFCs. Additionally, PFCs such as CF₄, C₂F₆, c-C₄F₈, and SF₆ persist in the atmosphere for thousands to tens of thousands of years [1], making any releases permanent on a human timescale (on the geologic timescale, human civilization emerged in the Holocene period covering the past 10,000 years to the present).

PFCs have been used in semiconductor fabrication facilities (fabs) because they provide uniquely effective process performance when etching high aspect ratio features and are a safer, reliable source of the fluorine needed for cleaning certain deposition process chambers.

In 1999, the WSC—whose members at the time were the European Electronic Components Manufacturer Association (now the European Semiconductor Industry Association [ESIA]), the Electronic Industries Association of Japan (now part of the Japan Electronics and Information Technology Industries Association [JEITA], as the Japanese Semiconductor Industry Association [JSIA]), the Korean Semiconductor Industry Association (KSIA), and the SIA—approved a consensus PFC emissions reduction goal [3]. That goal calls on WSC member associations to reduce aggregate absolute emissions of PFCs from semiconductor manufacturing facilities by 10% or greater from baseline levels by 2010. The baseline year for the ESIA, JEITA-JSIA, and SIA is 1995 while the KSIA baseline is 1997. The Taiwan Semiconductor Industry Association (TSIA) subsequently joined the WSC, which defined the baseline year for TSIA as the average of 1997 and 1999 emissions. It should be noted that the semiconductor industry, through the WSC, was the first industry to coordinate globally and voluntarily establish a greenhouse gas emissions reduction goal; moreover, the 10% goal exceeds the targets established by the Kyoto Protocol for any of the Annex I countries subject to specific greenhouse gas emissions reduction targets.

Concurrent with the establishment of the WSC goal, the U.S. semiconductor industry negotiated a second voluntary agreement with the EPA. The PFC Reduction/Climate Partnership Memorandum of Understanding (MOU) applies to U.S. semiconductor manufacturing operations only and supports the WSC agreement for a collective 10% reduction in emissions by 2010 [4].

Both the WSC consensus paper and the EPA memorandum of understanding call on semiconductor manufacturers to share pre-competitive information about potential PFC emission reduction processes and technology. The memorandum of understanding has an additional requirement that WSC partners publish a progress report by December 15, 2005, detailing progress towards achieving the 10% reduction goal.

This report documents pre-competitive information about potential PFC emissions reduction processes and technology obtained from ISMI, SIA, and WSC members. Additionally, information was gathered by written surveys of semiconductor manufacturers and suppliers as well as a review of relevant literature. Survey responses were received from 18 semiconductor manufacturers in the U.S., Europe, and Korea and from 14 suppliers based in the U.S., Europe, Japan, and Taiwan. Four WSC trade associations provided specific data while information for the fifth association was gathered from the 2005 International Semiconductor Environment, Safety, and Health (ISESH) conference proceedings. Emissions projections were developed based on VLSI Research, Inc. wafer demand historical data and projections through 2010. Normalized PFC emissions rates were calculated based on wafer demand data from Sage Concepts for Korea and Taiwan, and Dataquest for the U.S., Europe, and Japan.

This report reflects information available through July 2005. It is not intended to be a comprehensive summary of all PFC emission reduction activities. While attempts were made to include developments that occurred or were commercialized after the 1998 report, technologies may not be included if the users or developers did not disclose information for competitive or other reasons.

4 EMISSIONS REDUCTION TECHNOLOGY DEVELOPMENT

The semiconductor industry continues to employ a hierarchy in development of PFC emission reduction technology structured around the pollution prevention concepts of reduction, replacement, re-use/recycle, and abatement. These development areas are as follows:

- 1. Process optimization/alternative processing—reduces the amount of PFCs that are used and emitted
- 2. Alternative chemistries—reduces or eliminates emissions
- 3. Capture/recovery—re-uses or recycles PFCs
- 4. Abatement-destroys, reduces, or eliminates PFC emissions so they are not emitted

Certain technologies that were in research and development stages when ref. [1] was published have since been widely implemented by the industry; some technologies have been rejected because of poor performance or other issues; and new technologies are being developed and evaluated.

4.1 Process Optimization/Alternative Processing

Process optimization continues to focus primarily on CVD chamber cleans because they are historically the greatest source of PFC emissions; furthermore, they occur in the absence of wafers and can be optimized without negatively affecting product yield [4]. Cleans optimization can also be applied to etch and other process chambers where PFCs are used for in situ dry cleans. The PFC gases used in CVD chamber cleans include C_2F_6 and CF_4 in older (pre-1999) manufacturing equipment as well as C_3F_8 , C_4F_8 , octafluorotetrahydrofuran (C_4F_8O), and NF₃ that

are lower emitting C_2F_6 replacement chemistries. Based on 2004 emissions, C_2F_6 continues to be the primary chamber clean gas and currently makes up the majority of semiconductor PFC emissions. However, in terms of amounts purchased, NF₃ is fast catching up to C_2F_6 . In process optimization, endpoint detection or extractive metrology is used to monitor emissions and provide clean endpoint times that are minimized by adjusting process parameters such as chamber pressure, temperature, plasma power, cleaning gas flow rates, and gas ratios of mixtures. Cleans are optimized to minimize gas consumption, thereby lowering the cost of ownership (COO) due to decreased gas usage. Process optimization can yield emissions reductions of 10–56% compared to baseline C_2F_6 processes [5] with a potential benefit in throughput. Because of industry growth, optimization by itself has not achieved the levels of emission reduction the industry needs to meet the 10% goal; however, optimization can reduce emissions in older fabs and ensure that new chamber clean processes minimize gas consumption and operate efficiently.

4.2 Alternative Processing: Remote Clean

Alternative processing—replacing the original process with a new, lower emitting process—has undergone significant development in the last decade. The industry has developed remote plasma clean technologies to replace in situ C_2F_6 chamber cleans and CF_4 used in nitride chamber clean. Remote cleans dissociate NF₃ into fluorine ions (F⁺) or atoms in a remote plasma and then feed the F⁺ ions/atoms into the process chamber to remove silicon-based residues. Remote cleans convert NF₃ at 95–99% utilization efficiency [6]. Applied Materials has adopted remote plasma technology for chamber cleans across their advanced 200 mm and 300 mm CVD equipment line. Other companies have developed remote plasma technologies using NF₃ or other PFC chemistries that can be retrofitted to certain older CVD chambers. When compared to the original carbon-based PFC chamber cleans that they replace, retrofitted remote cleans result in >95% PFC emissions reduction [7]. Remote cleans also improve tool utilization by reducing clean times and wet clean frequency, improving mean time between failures (MTBF), and reducing costs of chamber parts. Additionally, they may improve yield through fewer defects.

4.3 Remote Clean Byproduct ESH Concerns

Implementing NF₃ remote cleans generates more fluorine (F₂) and hydrogen fluoride (HF) emissions than fluorocarbon-based cleans [8] and may require additional treatment to remove these gases from the exhaust stream, depending on the fab. Fabs typically treat F₂ and HF exhaust streams with water scrubbers; the additional loading on central end-of-pipe (EOP) scrubbers may require modifications to the scrubber systems or installation of point-of-use (POU) scrubbers. Depending on a fab's wastewater discharge limits, scrubber effluent may require treatment to decrease the fluoride loading. As noted by Vartanian et al.,

The existing wastewater and/or air pollution control approach and infrastructure may not be well suited to the increased F_2 load from NF₃-based chamber cleans. Thorough evaluation of the site's air pollution control strategy, existing wastewater handling/treatment infrastructure and capacity, and F_2 discharge limits should be completed before proliferation of NF₃-based chamber cleans [9].

Semiconductor manufacturer surveys indicate that other fabs have responded to similar challenges with remote NF_3 and the F_2 . Many fabs have existing fluoride waste treatment facilities that remove fluoride by precipitation with some form of calcium, generating calcium

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fluoride. Because of the significant reduction in PFC emissions and the process benefits, remote cleans are a key aspect of the industry's efforts to reduce PFC emissions; however, semiconductor manufacturers should take into account increased F_2 and HF loadings when developing air and wastewater treatment strategies.

4.4 Alternative Chemistry

Significant development has been made in alternative chemistries. Alternative chemistry, or chemical substitution, is the use of chemicals with lower global warming potential (GWP) or no GWP as an alternative to PFCs. Alternative chemistry also includes high GWP gases that are more efficiently used in plasma processes, thereby reducing overall greenhouse gas emissions. When evaluating alternative chemistries, criteria must include process performance, review of ESH risks, material availability and cost, and characterization of process emissions and byproducts. Fluorocarbons will generate CF_4 and possibly C_2F_6 and C_3F_8 byproducts when used in plasma processes; the amount of input chemical converted to a PFC byproduct must be quantified to ensure an accurate accounting of PFC emissions. Additionally, any fluorine-containing compound used in the presence of carbon in a plasma process, such as cleaning of an organic low-k deposition chamber, will form some quantity of PFC such as CF_4 and, possibly, C_2F_6 .

Since fluorocarbons appear to generate other PFCs and COF_2 while NF₃ increases F₂, HF, and NO_x emissions, focusing solely on reducing PFC emissions may generate additional ESH concerns.

4.4.1 Chamber Clean: ≤150 mm and Older 200 mm Process Tools

The predominant semiconductor PFC emission is C_2F_6 from CVD chamber cleans on ≤ 150 mm and older 200 mm process tools. C_2F_6 is used at 30% efficiency in typical chamber clean processes, resulting in 70% of the input gas being emitted [10]. Additionally, a typical C_2F_6 plasma chamber clean process converts ~10% of the input C_2F_6 into CF_4 on a mass per mass basis. As seen in Table 1, several replacements for C_2F_6 have been demonstrated and implemented in manufacturing fabs.

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction from Baseline C ₂ F ₆ Process
C ₃ F ₈	30–60	12–30 (CF ₄)	12–70
c-C ₄ F ₈	70–90	4–11 (CF ₄)	50–85
C ₄ F ₈ O	85–90	10–20 (CF ₄); 4 (C ₃ F ₈)	70–90
NF ₃	60–80	0–4 (CF ₄) depending on carbon content of film removed	20–90

 Table 1
 Implemented Alternative Chamber Clean Chemistries

 C_3F_8 , c- C_4F_8 , and C_4F_8O are drop-in replacements for C_2F_6 (i.e., new gas lines or additional ESH systems do not need to be installed). As Table 1 shows, significant amounts of CF_4 byproduct can be produced with the drop-in replacements; therefore, the amount of O_2 added to the clean process must be optimized to drive the reaction to COF_2 , a highly toxic but water-scrubbable byproduct, instead of CF_4 . Note that at least one semiconductor manufacturer has also identified the PFC byproduct C_3F_8 when using C_4F_8O . Whereas decreased COO is reported when using the

drop-in replacement chemistries in lieu of C_2F_6 (because of decreased clean gas consumption), the impact on emissions is variable. In addition to determining utilization efficiency, all of the PFC byproducts must be quantified to determine the total effect on emissions.

NF₃ is the most effective alternative chemistry currently used in manufacturing fabs when viewed in terms of clean time, carbon equivalent emissions (a metric used to compare different greenhouse gases based upon their global warming potential), and gas usage [11]. IBM implemented in situ NF₃ cleans to replace C_2F_6 at their Burlington, VT, manufacturing facility [12], and Novellus has developed dilute in situ NF₃ clean processes to replace C_2F_6 in their advanced 200 and 300 mm tools [13]. However, NF₃ is not a drop-in replacement. Unlike the fluorocarbon alternative chemistries in Table 1, NF₃ is an oxidizer. The use of NF₃ precludes the generation of fluorocarbon byproduct unless organics are present; however, plasma chemistries are complex and use of an in situ NF₃ clean process may increase emissions of HF and F₂ as well as NO_x. Additional ESH controls, such as local scrubbing, may be required; additionally, one semiconductor manufacturer recommended installing a coated stainless steel exhaust duct [7]. On a mass basis, NF₃ has a higher cost per kilogram than C_2F_6 and the other fluorocarbon replacements; however, that cost may be offset by decreased consumption and faster clean times.

 CF_4 is used in certain older plasma enhanced (PE)CVD silane deposition chambers for chamber cleaning. One semiconductor manufacturer reported using C_2F_6 as an alternative chemistry, reducing PFC emissions by >57% from the baseline CF_4 process.

4.4.2 Chamber Clean: Advanced 200 mm and 300 mm

Because of significantly lower PFC emissions and process benefits, CVD tool supplier Applied Materials has standardized remote NF_3 cleans for their advanced 200 mm and 300 mm tools while Novellus has adopted in situ NF_3 cleans for their corresponding tools. Remote plasmas use NF_3 with 95–99% efficiency, whereas in situ processes use NF_3 with 60–80% efficiency [14]. The lower utilization efficiency of in situ cleans may require additional abatement; however, NF_3 is abated with most PFC abatement technologies. Destruction-removal efficiencies of 95–99.9% have been reported.

4.4.3 Chamber Clean: Research and Development

Several chamber clean chemistries are in research and development. From 1998–2002, Japan's Research Institute of Innovation Technology for the Earth undertook an effort to identify alternative chamber clean chemistries, eventually recommending carbonyl fluoride (COF₂) as a replacement gas. With a GWP of 1 [15], COF₂ has a much lower global warming potential than other fluorocarbons used for chamber cleans, and, although COF₂ is toxic, it is easily removed from the exhaust stream by water scrubbing. At the 12th ISESH Conference in 2005, JEITA-JSIA members presented results of COF₂ evaluations in manufacturing environments. COF₂ cleans reduced PFC emissions 96% with process performance equivalent to PFCs [16] [17]; however, at a cost of 20,000Yen/kg (~\$175/kg), COF₂ is currently not a cost-effective alternative.

Chlorine trifluoride (ClF₃) was mentioned in the 1998 report as a potential alternative chamber clean gas for polysilicon and nitride chambers. Although ClF₃ has no GWP or ozone depletion potential, it has not been widely adopted in the industry because of its extreme reactivity and the risks and costs associated with safe storage and use. In fact, efforts have been undertaken to replace ClF₃ with alternative chemistries such as NF₃ and fluorine [18].

Fluorine (F_2) has been discussed as a possible alternative to PFCs for CVD chamber cleaning but was not considered a serious alternative in the past because of the ESH risks associated with

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transport, storage, and use of high pressure F_2 cylinders. These problems have been addressed by two companies that have developed POU fluorine generators [19][20]. POU F_2 generators convert anhydrous HF into F_2 by electrolysis. After the F_2 is generated, it is purified to remove residual anhydrous HF and other contaminants. While anhydrous HF is toxic and corrosive and F_2 is highly toxic and a strong oxidizer, neither of these materials are global warming gases. When used to clean organic low-k deposition chambers, F_2 generates a small quantity of PFC byproduct such as CF_4 .

4.4.4 Plasma Etch

While replacing high GWP gases with lower or non-GWP gases is generally preferable, it has not proven feasible in most plasma etch applications. Processing requirements for high aspect ratio plasma etching continue to become more stringent, requiring both fluorine to etch and the right carbon-to-fluorine ratio to ensure anisotropic etching. While a significant amount of research has been done on alternative etchants such as iodofluorocarbons, hydrofluorocarbons, and unsaturated fluorocarbons [21]–[24], many of these chemicals are not feasible alternative etchants in a manufacturing environment because of excess polymerization, lack of etch selectivity, difficulties in delivering gases to the process chamber, and potential increased employee exposure risks. An exception is hexafluoro-1,3-butadiene (C_4F_6) for oxide and low-k etching where high selectivity to silicon is required in the presence of nitride or other films with high aspect ratios, thinner resists, and less etch resistant resists. In these cases, C_4F_6 replaces CF_4 , CHF_3 , and C_4F_8 [24]. With an atmospheric lifetime <1 year and utilization efficiency >95%, PFC emissions can be reduced by >90% compared to baseline CF_4 , CHF_3 and C_4F_8 processes [26]; however, as is the case with all higher molecular weight fluorocarbon compounds used in plasma processes, some CF_4 byproduct is formed and emitted.

4.5 Capture/Recovery

Several semiconductor manufacturers and suppliers conducted alpha and beta evaluations of PFC capture/recovery systems that could be installed as a central, building-wide means for handling PFC emissions [26]–[30]. Technologies evaluated include membrane separation, cryogenic recovery, and pressure swing adsorption/desorption. No evaluation resulted in successful re-use of PFC; all were deemed to be too costly to implement. Capture/recovery technology requires extensive pretreatment of the process tool exhaust stream to remove corrosives, pyrophorics, moisture, and particulate. Historically, chamber clean PFCs make up the majority of PFC emissions. As NF₃-based cleans proliferate, large building-wide capture/recovery systems become less cost-effective due to the reduced volume of PFCs available for recovery. To date, no semiconductor facility in the world has successfully implemented centralized capture/recovery technology.

As new, lower emitting chamber cleans are implemented and older fabs are decommissioned, the mix of PFC emissions is expected to change. JEITA-JSIA projects that, in 2010, the largest quantity of PFC emitted from Japan's semiconductor facilities will be SF₆. In addition to plasma etch processes, SF₆ can be found in specialized processes such as IC testing and wafer thinning where it is used in large volume. Air Liquide presented data on a semi-centralized membrane system used to capture and recycle SF₆ [31]. In the Air Liquide application, SF₆ was being used in large volume as a blanket gas, not as a plasma etchant. Byproducts requiring pre-treatment were not present in the exhaust stream; therefore, SF₆ could be captured and re-used in the process, thus reducing process cost of ownership due to reduced virgin SF₆ purchases. While centralized capture/recovery does not appear to be a cost-effective way to reduce PFC emissions,

smaller capture/recovery systems may be appropriate, as demonstrated in the Air Liquide case, for niche, single PFC, high volume processes.

4.6 Abatement

Since the publication of ref. [1], many new PFC abatement technologies have been developed and new systems commercialized. The industry has favored POU over centralized EOP abatement for PFCs, believing that it is more effective to abate close to the source and, thus, before dilution; however, one semiconductor company has recently installed an EOP abatement system that uses corona discharge plasma technology to destroy PFCs from CVD chamber cleans. Most abatement technologies can be applied to PFC emissions from both etch and CVD processes, although several companies have developed plasma abatement systems specifically for etch chamber emissions. These are typically installed before the vacuum pump (i.e., the foreline) to avoid dilution of the stream with pump-purge N₂. Because it is desired to abate certain CVD processes for deposition gases, some semiconductor manufacturers have elected to install POU abatement technology that can also abate PFC emissions.

As noted earlier, fluorocarbons will generate CF_4 and possibly C_2F_6 and C_3F_8 byproducts when used in plasma processes. Additionally, the use of any fluorine-containing compound in the presence of carbon in a plasma process will form some quantity of CF_4 . Certain abatement devices sold for PFC applications are not capable of destroying CF_4 effectively.

Abatement manufacturers may use different methods of determining destruction/removal efficiency (DRE) because the industry has not developed a standardized method. This can make a direct comparison of abatement technologies difficult. Performance of abatement systems varies greatly depending on a variety of abatement device and process parameters such as temperature, PFC inlet concentration, flow rate, overall inlet stream composition, etc. In addition, consumables, maintenance, and utilities have a significant impact on COO.

Technologies under development or proven to be effective in abating PFC emissions from specific applications are listed in Table 2.

Technology Type	Description and Applicability
POU Fueled Burner – Scrubber	Uses a propane, methane, natural gas or hydrogen flame to destroy PFCs and other hazardous substances such as deposition precursors followed by a water scrubber, which may contain a base solution, to remove volatile acid gases from the exhaust stream. May not be effective in abating CF ₄ . Burner- scrubber units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of N ₂ that can lower the combustion unit temperature and, thus, DRE. Burner- scrubber units can typically abate emissions from multiple process chambers. Except for the hydrogen-fueled devices, they all generate additional greenhouse gases in the form of CO ₂ .
POU Catalytic – Scrubber	Uses a catalyst to promote the destruction of PFCs and process gases at lower activation energies than would otherwise be needed. Catalytic systems operate at a lower temperature than other PFC abatement systems, are electrically heated, and do not require a fuel. A water scrubber typically follows the catalytic reactor to remove HF byproduct from the exhaust stream. May not be effective in abating CF ₄ . Catalytic scrubber units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of nitrogen. Catalytic scrubber units can typically abate emissions from multiple process chambers.

Table 2PFC Abatement Technologies

Technology Type	Description and Applicability
POU Electrically Heated Thermal – Scrubber	Uses an electrically heated chamber to destroy PFCs and other hazardous substances such as deposition precursors, followed by a water scrubber to remove volatile acid gases from the exhaust stream. Electrically heated thermal-scrubber units are installed on the process tool exhaust line after the vacuum pump. May not achieve the high temperatures required to effectively abate CF_4 . Electrically heated-scrubber units can typically abate emissions from multiple process chambers.
POU Atmospheric Plasma	Uses plasma to destroy PFCs and other hazardous substances such as deposition precursors. The plasma chamber can be followed by a water scrubber, which may contain a base solution, to remove volatile acid gases from the exhaust stream. Atmospheric plasma units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of nitrogen, which can impact the plasma efficacy. Atmospheric plasma units are typically designed to abate emissions from multiple process chambers.
POU Pre-pump Plasma	Point-of-use foreline plasma units employ a compact, low-pressure plasma reactor to destroy PFCs from etch processes. Foreline plasma units are installed on the foreline after the turbo pump but before the mechanical vacuum pump, where they can abate concentrated emissions before dilution with N_2 purge from the vacuum pump. One unit is required for each etch process chamber.
Centralized Atmospheric Plasma	The only centralized PFC abatement system is the corona discharge system jointly developed by FH Co., Ltd and Samsung Electronics in Korea. A separate PFC exhaust line is installed post-vacuum pump to segregate CVD chamber clean emissions from deposition emissions. The PFC exhaust passes through the annular space between co-axial cylindrical electrodes used to sustain a corona discharge at atmospheric pressure. Exhaust from the abatement system then flows to the house scrubber for removal of acid gases.

5 INDUSTRY APPLICATION OF EMISSION REDUCTION OPTIONS

The age, size, and infrastructure of a fab are the factors that have the greatest impact on the applicability of PFC emission reduction technology. For instance, older fabs process smaller wafers, are typically smaller in size, and may have space and infrastructure constraints such as a lack of or undersized utilities required to support specific reduction technologies; moreover, manufacturers of the process tools in older fabs are typically no longer supporting those tools with new process development. WSC member companies were surveyed to determine the technologies that they are implementing to reduce emissions. Table 3 summarizes the PFC emissions reduction options the industry is applying to fabs processing various wafer sizes.

Tool Type	≤150 mm Fabs	Old Technology 200 mm	Advanced 200 mm and 300 mm
	Fab Decommission	Process Optimization	NF ₃ -based Cleans
	Process Optimization	Endpoint Detection	F ₂ Cleans
CVD	Endpoint Detection	Remote NF ₃ Cleans	Endpoint Detection
	Alternative Chemistries	Alternative Chemistries	Abatement
	Limited Abatement	Abatement	
	Fab Decommission	Limited Abatement	Alternative Chemistries
Etch		Limited Capture/Recovery	Abatement
			Limited Capture/Recovery

Table 3PFC Emissions Reduction Options

The industry is steadily decommissioning $\leq 150 \text{ mm}$ fabs, eliminating them as a source of PFC emissions. The $\leq 150 \text{ mm}$ fabs that continue operations may have few choices of emissions reduction technologies because of space and infrastructure constraints. For $\leq 150 \text{ mm}$ fabs, process optimization and drop-in alternative chemistries for CVD cleans may be the only alternatives for reducing emissions, although a few $\leq 150 \text{ mm}$ fabs have installed abatement on certain CVD processes.

For older 200 mm fabs with CVD tools using C_2F_6 cleans, the industry has focused their PFC reduction efforts on CVD emissions. Process optimization, installation of endpoint detection, installation of remote NF₃ cleans, and alternative clean chemistries are the most prevalent means of reducing emissions. One company reported installing abatement in an older 200 mm fab; however, abatement typically requires floor space that may be limited in an existing fab and could require facilities services that are not available. If etch emissions abatement is also needed, the small footprint pre-vacuum pump plasma systems may be the only alternative to reduce emissions. Capture/recovery may be appropriate for specialized high volume PFC applications.

Based on the survey, the industry and its suppliers have integrated low emission CVD tools into advanced 200 mm and 300 mm fabs. If an advanced CVD tool uses silane or other flammable or pyrophoric precursors and in situ NF₃ cleans, burner-scrubber abatement with high DREs for all these emissions is available and in use in some fabs. Companies also report using endpoint detection to minimize PFC gas consumption. With the advent of low emission clean processes, 300 mm etch is expected to gain an increasing share of the industry's total PFC emissions. Some companies report using alternative etch chemistries to reduce emissions; however, implementation of alternative etchants as a retrofit is costly and time-consuming. Because etch occurs on the wafer surface, process changes require extensive evaluation and process requalification before implementation. Several companies report using abatement technologies to reduce etch emissions in their advanced 200 mm and 300 mm fabs, and one company is using a central EOP plasma unit to abate CVD emissions from an advanced 200 mm fab. Additionally, capture/recovery may be appropriate for specialized high volume PFC applications.

6 IMPACT OF INDUSTRY CHANGES ON EMISSIONS

Since publication of ref. [1], the industry has undergone significant changes that impact PFC emissions. These changes include development and implementation of new chamber clean processes and chemistries, increased use of plasma etching and adoption of new etch gases, development of new materials and processes, and larger wafers to manufacture advanced semiconductor devices.

6.1 Chamber Cleans

The impact of NF₃ cleans is realized principally in advanced 200 mm and 300 mm fabs; however, in 2004, ~66% of the total silicon demand was processed in older technology fabs (\leq 150 mm and older 200 mm) using fluorocarbon-based cleans. In fact, C₂F₆ still accounted for ~48–50% of the industry's total PFC emissions in 2004 [33]. A transition from C₂F₆ cleans to alternative processes and chemistries is evidenced by some associations reporting reductions in C₂F₆ emissions and increasing NF₃ or C₃F₈ emissions. Note, however, that the associations that reported increased C₃F₈ emissions in 2004 also reported increases from 2003 levels in overall PFC emissions, despite the transition to C₃F₈.

6.2 Etch

In interviews, semiconductor etch professionals [33] provided input on PFC usage in etch over time. They agreed that the move from 200 mm to 300 mm equipment has resulted in a 1.5–2X increase in etch PFC consumption per wafer pass; however, they noted that the increased usage is less than would be expected based on the 2.25X increase in wafer area.

The increase in microprocessor metal levels from four in 1995 to 11 in 2004 has led to an increase in back-end etch PFC usage. Due to requirements for higher selectivity to resist and underlying films, c-C₄F₈ and C₄F₆ are now being used more extensively for dielectric etching, replacing CHF₃ and CF₄. Both chemistries generate C₂F₄, CF₄, C₃F₈, C₂F₆, CHF₃, and some C₄F₈ byproducts; however, MIT and Motorola's Semiconductor Product Sector (now Freescale Semiconductor) demonstrated equivalent process performance and a 65–82% reduction in PFC emissions for organosilicate glass and oxide etching when using C₄F₆ in lieu of c-C₄F₈ [34]. Experts note that as device line and contact sizes are scaled, the aspect ratio remains the same; therefore, films are becoming thinner and etch times shorter, thereby decreasing PFC usage. However, one expert cautioned that selectivity requirements are becoming more critical with the thinner layers and required process changes may result in increased PFC consumption over time. The impact of ultra low-k dielectrics on PFC emissions cannot be ascertained at this time because it is too early in their development stage.

In the front-end, integrations using multiple spacers and sometimes multiple polysilicon layers have increased PFC usage. As high-k dielectrics and gates are implemented, increased etching could further increase PFC consumption. It is too early to quantify the impact of novel structures such as FinFET on PFC emissions.

In recent years, semiconductor tool suppliers have evaluated in situ cleans or dry cleans for etch tools to maximize tool uptime and increase mean time between wet cleans (MTBC) [35]. While oxygen can be used to clean organic byproducts of the resist from the chamber walls, fluorine-containing gases are required to remove silicon-based residues. The use of in situ cleans is likely to increase PFC emissions from etch tools.

One etch expert estimates that the industry can anticipate a net 2% increase in PFC consumption and, therefore, emissions each year [36]. With increasing usage of NF₃-based cleans in 300 mm fabs, etch will become a significant source of 300 mm PFC emissions.

6.3 Future Technologies That May Impact PFC Emissions

Atomic layer deposition (ALD) is used increasingly in the industry to deposit back-end copper barriers and seed layers. In the front-end, ALD is being used to deposit metal gates and high-k dielectrics. These materials replace films that formerly were deposited by diffusion processes that did not have PFC chamber cleans. In situ and remote plasma NF₃-based chamber cleans are currently in development to replace cleans that require the chamber be taken down to remove parts. Non-PFC chemistries are also being evaluated for in situ or remote plasma chamber cleans.

Finished semiconductor wafers contain multiple computer chips called dies. The finished dies are cut, packaged, and then sent to manufacturers to integrate into products such as cell phones, computers, personal music players, and automobiles. The shrinking size of electronic products requires that packaged integrated circuits be reduced in thickness and footprint. Thin IC packages require thinner dies; additionally, fully depleted silicon on insulator (SOI) used for low power, high speed devices also requires thinning of SOI wafers. The four major methods of reducing die thickness are mechanical grinding, chemical mechanical planarization (CMP), wet

etching, and atmospheric downstream plasma (ADP) etching [37]. ADP etching requires PFCs; however, it is not certain that ADP will be the technology of choice for wafer thinning.

3D interconnect—stacking chips and connecting them through vias on the die—is a technology being pursued to shorten interconnects and decrease delay time [38]. 3D interconnects will employ wafer and die thinning technology, but those are most likely to be wet chemical- or CMP-based. The technology will require an additional metal deposition; however, it is hoped that new architecture will eliminate an existing layer of metal and the metals changes will be PFC-neutral. An additional etch step is required, but again chip redesign is anticipated to eliminate levels and reduce etch process steps.

6.4 Changes in Wafer Size

12

The change with the largest impact on PFC emissions over time is increasing wafer size and the corresponding advanced processing technologies. Older technology ≤150 mm wafers constituted the bulk of wafer demand in 1995. Between 1995 and the present, ≤ 150 mm wafer demand has steadily declined. VLSI Research projects that ≤150 mm wafer demand will be 54% below 1995 levels in 2005 and 73% below those levels in 2010 [40]. Nine semiconductor manufacturers (1 based in Europe, 2 in Korea, and 6 in the U.S.) provided information on actual and projected PFC emissions per fab type in 1995, 2000, 2005, and 2010 [41] While all nine companies indicated PFC emissions from ≤150 mm fabs in 1995, five were emitting PFCs from those fabs in 2005 and only four expect to be emitting PFCs from ≤ 150 mm fabs in 2010. Both the industry survey results and VLSI Research wafer demand projections are clear indicators of the industry trend to close and decommission older technology fabs. PFC emissions increased between 1995-2000 as first generation 200 mm fabs using predominantly C_2F_6 cleans ramped up; 200 mm wafers became the predominant wafer type by 2000. As advanced 200 mm and 300 mm wafer fabs began ramping in 2001–2004, the normalized rate of emissions (PFC emitted/ cm^2) decreased, most likely due to use of NF₃-based chamber clean processes. An estimate of the percentage of 200 mm wafer demand attributable to older technology fabs versus advanced fabs can be made by assuming that the additional demand above 1999 levels is due to advanced fabs. Based on these estimates, worldwide, advanced 200 mm and 300 mm fabs will account for approximately 70% of semiconductor manufacturing wafer demand in 2010 [41][42] (Figure 1).

The semiconductor industry has experienced significant growth from 1995 to 2004 with wafer demand increasing 52% [42]. As seen in Figure 2, while silicon demand has increased, PFC emissions per square inch of silicon increased from 1995–2000 and then began decreasing from 2001–2004. The decreasing trend can be explained by the transition to advanced 200 mm and 300 mm wafer fabs coupled with a change in chamber cleaning technology between older and newer fabs. Newer fabs employ NF₃-based cleans that result in much lower PFC emissions than C_2F_6 cleans. If older manufacturing facilities are shut down, C_2F_6 -based cleans will be reduced. Based on the changes brought about by the shift to larger wafer sizes and the accompanying transition from old technology to new, trends indicate that the normalized rate of PFC emissions will continue to decline through 2010.

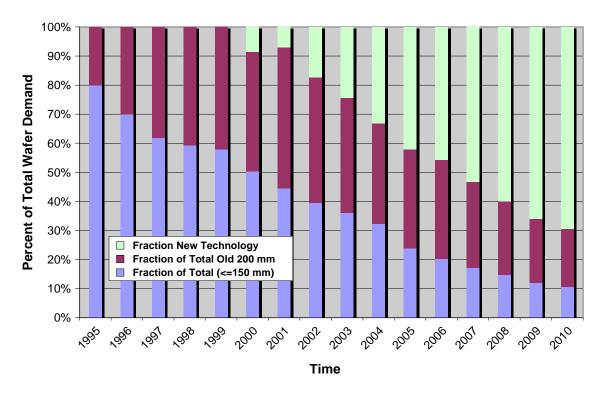


Figure 1

1 Wafer Demand Over Time (1995–2010)

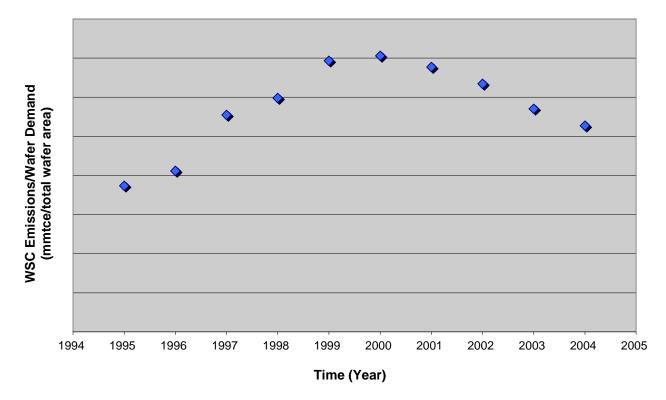


Figure 2 WSC Production Normalized PFC Emissions Over Time

7 SIA PROGRESS TOWARDS 10% EMISSIONS REDUCTION GOAL

The SIA partners have achieved significant reductions in PFC from their 1999 peak level emissions, meeting the 10% goal in 2003 and exceeding the goal in 2004 (Figure 3). SIA reductions have been achieved through process optimization, alternative processes, alternative chemistries, and abatement. In addition, some older fabs have been closed while some newer fabs have been built that use lower emission technologies and more abatement.

While much has been written about the shrinking of the U.S. semiconductor industry, SIA reductions are not due solely to fab closures. From 1995–2004, North American fabs increased wafer demand by 55% as measured in wafer area [42] in spite of fab closures.

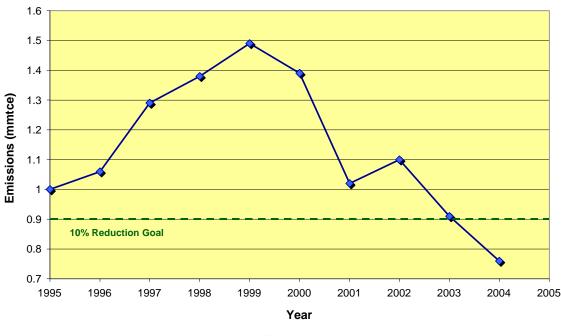


Figure 3 Annual SIA PFC Partner Emissions

8 PROJECTED WSC EMISSIONS

All of the associations are demonstrating a decrease in normalized emissions (million metric tons of carbon equivalent [MMTCE]/square inch of wafer demand); however, absolute emissions in 2004 are 0.5–1.3X for four of the five associations. The industry has consistently reduced PFC emissions per square inch of silicon since 2000 (Figure 2). A linear regression analysis of the 2001–2004 normalized emission data results in an R-squared value of 0.99. Assuming this trend continues, emissions can be projected through 2010 using a linear extrapolation. Figure 4 shows historical WSC-indexed emissions, as well as projected WSC-indexed emissions from 2005–2010, based on this linear extrapolation and VLSI Research, Inc. wafer demand projections. Indexed emissions are actual emissions divided by the WSC 2010 goal. An index value of 1.0 is equivalent to the 2010 goal. Because KSIA and TSIA joined the WSC after 1995, their emissions are not included in 1995 and 1996, resulting in indexed emissions for those years that are less than the overall WSC goal. While VLSI Research predicts increased wafer demand from 2005–2009, the predicted demand is expected to decrease from 2009 to 2010. Assuming the normalized emissions rate trend continues and that VLSI's projected demands are accurate, WSC emissions are projected to be lower than the 2010 reduction goal.

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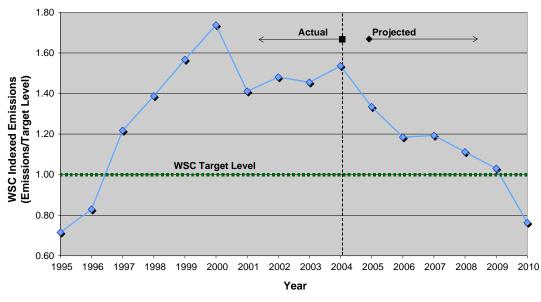


Figure 4 WSC Indexed PFC Emissions – Actual and Projected

9 DISCUSSION AND ANALYSIS

Following the pollution prevention hierarchy, many technologies have been developed in recent years to reduce PFC emissions. Based on the current state of those technologies as described in this report, several factors related to their applicability and implementation should be considered.

9.1 Applicability of Technologies

The applicability of PFC emission reduction technology depends on the age, size, and infrastructure of a fab. In 2004, the largest PFC emission continues to be C_2F_6 , at 48–50% of total semiconductor PFC emissions. C_2F_6 emissions are expected to decrease over time as 300 mm fabs with NF₃- and F₂-based cleans ramp up and as older fabs shut down.

For older fabs that will continue operations beyond 2009, companies may want to

- Implement those alternative clean processes and chemistries that achieve the highest levels of emissions reductions, or
- Install abatement, if feasible.

Due to projected growth in 300 mm fabs, careful monitoring of 300 mm PFC consumption and CVD and etch emissions from those fabs as they ramp up are recommended. If a company's 300 mm fabs use CVD chamber clean technologies other than remote NF_3 or F_2 cleans, the amount of CVD PFC emissions need to be evaluated to determine if additional measures should be implemented to further reduce emissions.

Etch emissions are expected to grow over time and may become the major source of 300 mm PFC emissions. Because etch processes are already optimized to achieve the required process performance, alternative chemistries and process optimization are typically not feasible. Abatement may be the only option if further emissions reductions are needed.

9.2 Process Optimization/Alternative Processing

By itself, process optimization may not reduce emissions sufficiently to enable industry associations to meet the goal. Because of other benefits including cost reduction and pollution prevention, however, it should be used on all CVD chamber cleans to minimize chemical consumption and waste generation.

The alternative process remote cleans minimize PFC emissions. Additionally, they may offer process, yield, and COO benefits. In older fabs, replacing C_2F_6 cleans with options such as remote cleans, in situ NF₃ cleans, or alternative chemistries is likely to be the most cost-effective means to minimize PFC emissions. The impact of increased F₂ emissions must be addressed when designing exhaust systems and wastewater treatment systems.

9.3 Alternative Chemistries

Alternative chemistries are being used to replace C_2F_6/O_2 chamber cleans in older process tools. These chemistries must be chosen carefully to ensure tangible benefits. One WSC member association has shown a substantial increase in C_3F_8 emissions over time with a concurrent reduction in C_2F_6 emissions; however, total emissions of C_2F_6 and C_3F_8 in 2004 exceed the highest historical C_2F_6 emission. This may indicate the C_3F_8 does not provide the level of emissions reduction needed to reduce overall emissions in line with the growth of wafers processed.

When evaluating alternative chemistries, criteria must include the following:

- Process performance
- Review of ESH risks
- Alternative chemistry availability and cost
- Process emissions and byproducts characterization

Choosing an alternative based solely on its utilization efficiency may raise additional ESH concerns. For example, fluorocarbon-based alternatives generate difficult-to-abate CF_4 byproducts and, potentially, other fluorocarbon byproducts. The use of NF₃ generates increased F_2 , HF, and NO_x emissions. While resulting in minimal PFC emissions, F_2 is highly toxic and reactive, thus requiring significant ESH controls, such as double contained piping, toxic gas monitoring, abatement, and possibly upgrading of exhaust ducts.

While alternative etchants have been extensively researched, C_4F_6 appears to be the only alternative evaluated so far that provides the required process performance while reducing emissions.

9.4 Capture/Recovery

Although centralized capture/recovery has not proven cost-effective, smaller capture/recovery units may be appropriate in specialized cases when a process uses a single PFC in large volume without plasma processing, resulting in emissions of a high volume, relatively clean PFC stream.

9.5 Abatement

The number and type of commercially available PFC abatement systems has increased dramatically since the first *Current State of Technology: Perfluorocompound (PFC) Emissions*

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Reduction [1] report was issued. Abatement devices range from those that are commercially available with hundreds installed in semiconductor applications to alpha and beta units. Some abatement devices can be used only in specific applications. DRE and COO can vary greatly from one abatement device to another.

When using PFC abatement, semiconductor manufacturers should establish performance standards for the following:

- Maximum downtime allowable
- COO
- Minimum DRE

Abatement devices typically have consumable parts that must be replaced; the parts requiring replacement, frequency of replacement, and equipment downtime costs should be understood.

Because a standard method to calculate DRE does not currently exist, comparing the results of one abatement device to another is difficult. Many abatement technologies use additives that dilute the exhaust stream; these additives must be taken into account by determining the total dilution across the system. Semiconductor manufacturers must ensure that a PFC abatement device is capable of performing in the specific application for which it is required. DRE data generated from an abatement device installed on a 200 mm etch process are not likely applicable to the same etch process on a 300 mm tool because of increased PFC gas flows and other process variations. Additionally, the total amount of exhaust flow through an abatement device can vary from one application to another.

Fluorocarbons in plasma processes can generate a significant amount of CF_4 . When installed on fluorocarbon processes, the ability of an abatement device to abate CF_4 must be understood; moreover, to minimize total PFC emissions, the device must effectively abate CF_4 , the PFC most difficult to abate.

Finally, once installed, semiconductor manufacturers must ensure that PFC abatement devices are operated and maintained according to the abatement device manufacturer's specifications to ensure that DRE is maintained over time.

9.6 Impact of New Process Technology

It is not anticipated that new processing technologies will have a significant impact on PFC emissions before 2010; however, they do have the potential to impact emissions beyond 2010. Thus, it is recommended that the industry monitor the development and implementation of manufacturing technologies such as wafer thinning, ALD, and in situ dry cleans as well as new front-end integrations and materials and 3D interconnects. If possible, these technologies should be developed without using PFCs or by using those PFCs and processes that result in the lowest levels of emissions; however, new manufacturing technologies may not be possible without PFCs.

If new technologies require PFCs, processes should be developed that

- Minimize the amount of PFC required
- Maximize PFC utilization efficiencies
- Minimize formation of PFC byproducts

If PFC emissions from these new technologies become significant, efforts should be made to employ capture-recovery (for high volume streams) or to abate emissions.

10 CONCLUSIONS

As the first industry to coordinate globally and establish a voluntary greenhouse gas emissions reduction goal, the semiconductor industry has established itself as a leader and model for other industrial sectors. The world semiconductor industry has demonstrated significant commitment to reducing PFC emissions. The U.S. semiconductor industry achieved the 10% reduction goal in 2003 and surpassed the goal in 2004, despite a significant increase in wafer demand over time. If the current normalized PFC emissions trend continues and wafer demand projections are accurate, the world-wide industry will achieve the 2010 goal; however, these trends and projections largely depend on the ramping up of lower emitting advanced 200 mm and 300 mm fabs and a decrease in the emissions from older, higher emitting fabs.

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APPENDIX A – Process Optimization/Alternative Processing

A.1 Process Optimization

Process optimization uses extractive metrology such as mass spectrometry (MS) and Fouriertransform infrared spectroscopy (FTIR) to monitor emissions and provide clean end point times that are minimized based on process parameters such as chamber pressure, temperature, plasma power, cleaning gas flow rates, and ratios in the case of mixtures. Chamber cleans are optimized to minimize gas consumption, thereby, lowering cost of ownership (COO) and reducing perfluorocompound (PFC) emissions. Cleans optimization is primarily applicable to chemical vapor deposition (CVD) chambers, but the technology can also be applied to etch and other process chambers where PFC cleans are performed on a regular basis.

• Technology Status

Process optimization can be completed with internal company resources, if available, or by contract.

• Applicability

Chamber cleans optimization is applicable to ≤ 150 mm, 200 mm, and 300 mm CVD reactors and to other process tools using regular PFC chamber cleans. A significant amount of work has been previously published on optimization of Novellus Concept One and Applied Materials P5000 chamber cleans.

- Pros
 - In addition to reducing PFC emissions by up to 50%, process optimization requires no capital and results in decreased COO (up to 50%) due to reduced chemical usage and increased throughput.
- Cons
 - Process requalification may be necessary.
- Reported Results

Clean Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
C_2F_6	33–55	7–30 (CF ₄)	20–50
NF_3 (in situ)	60 → 70	0–4 (CF ₄) Depending on carbon content of film removed	20–40
NF ₃ (remote)	> 98	0–4 (CF ₄) Depending on carbon content of film removed	>95–99

• Cost of Ownership

COO reductions of 20-50% are achievable.

• Recent Publications on PFC Process Optimization

- G. Loh, Y. Osaki, and M. Mocella, "Perfluorocompound (PFC) Emission Reduction in Existing Plasma Enhanced Chemical Vapor Deposition (PECVD) Tools," *Proceedings* of the 11th ISESH Conference, PFC paper #2, 2004.
- A.D. Johnson, R.V. Pierce, M.I. Sistern, M. Kencel, R. Sward, and H. Winzig, "<u>C2F6-based</u> <u>Chamber Clean for Silane Plasma Enhanced Chemical Vapor Deposition (PECVD)</u>, International Semiconductor, 27 (3), p.57, March, 2004.
- Y-d Yoo, "Perfluorocompound (PFC) (C₃F₈) Emission Reduction by Optimizing Cleaning Process," *Proceedings of the 10th Annual ISESH Conference*, 2003.
- A.D. Johnson, R.G. Ridgeway, and P.J. Maroulis, "<u>Reduction of Perfluorocompound (PFC)</u> <u>Emissions to the Environment Through Advances in Chemical Vapor Deposition (CVD)</u> <u>and Etch Processes</u>," *IEEE Transactions on Semiconductor Manufacturing*, 17, p.491, 2004.
- V. Vartanian, B. Goolsby, R. Chatterjee, R. Kachmarik, D. Babbitt, R. Reif, E. Tonnis, and D. Graves, "<u>Reduction of Semiconductor Process Emissions by Reactive Gas</u> <u>Optimization</u>," *IEEE Transactions on Semiconductor Manufacturing*, 17, p.483, 2004.

• Contacts

Robert Ridgeway, Air Products and Chemicals, Inc., 610-481-4436, ridgewrg@airproducts.com

Gary Loh, DuPont, 302-999-4971, gary.loh@dupont.com

References

Information on process optimization was provided by SIA member companies including Laura Mendicino of Freescale Semiconductor, by Francesca Illuzzi of STMicroelectronics, Robert Ridgeway of Air Products & Chemicals, Inc. and Gary Loh of DuPont.

A.2 Endpoint Detection

• General Technology Description

Endpoint detection uses techniques such as MS, infrared (IR) spectroscopy, optical emission spectroscopy (OES), and radio frequency (RF) impedance monitoring to monitor changes and provide plasma process end point times. PFC gas consumption and emissions can be minimized by determining chamber clean end points and optimizing process parameters such as chamber pressure, temperature, plasma power, cleaning gas flow rates, and ratios in the case of mixtures. Endpoint detection has been used extensively for CVD chamber cleans, but the technology can also be applied to etch and other PFC plasma processes.

• Technology Status

Commercially available for use in ≤ 150 mm, 200 mm, and 300 mm CVD and etch reactors. Many process tool suppliers offer supplier supported endpoint detection systems and processes. Endpoint detection can also be installed as a retrofit.

• Applicability

Endpoint detection is applicable to \leq 150 mm, 200 mm, and 300 mm CVD and etch reactors.

Technology Transfer #05104693A-ENG

• Pros

- Reduced PFC emissions due to decreased process time.
- Decreased COO.
- Possible increase in process throughput.

• Cons

- As a retrofit, endpoint detector must be purchased and installed which could require capital expenditure.

Reported Results

An un-named SIA member company reports 40% PFC emissions reduction from baseline process for ≤ 150 mm and 200 mm Applied Materials and Novellus C₂F₆-based cleans. Philips reports PFC emission reductions of 29–53% and C₂F₆ gas usage reductions of 34–47% on borophosphosilicate glass from a TEOS oxysilane source (BPTEOS), undoped silicate glass (USG), and SiN clean processes

• Recent Publications

R. Dam, "Optimization of C₂F₆-based Plasma Enhanced Chemical Vapor Deposition (PECVD) Chamber Cleaning Process Minimizing Perfluorocompound (PFC) Emissions and Operating Costs on a Novellus C-2 Platform," *Proceedings of the 10th Annual ISESH Conference*, (2003).

References

Information provided by Harry Thewissen of Philips and an SIA member company.

A.3 Remote Plasma Cleans

• General Technology Description

Remote plasma clean technology was developed as an alternative to in situ CVD chamber cleans to clean the deposition byproducts left in the chamber after wafer processing. With remote chamber clean, a plasma-generating unit is mounted on the lid of a CVD chamber. Remote cleans typically react NF_3 or C_3F_8 in a plasma. The fluorine radicals and ions generated in the remote plasma unit are routed to the processing chamber where they chemically react with deposits. The deposition byproducts are then carried away in gaseous form, e.g., SiF₄.

• Applicability

This technology is commercially available for 200 mm and 300 mm CVD chamber cleans. Remote cleans is the process of record (POR) for Applied Materials advanced 200 mm and 300 mm PECVD chamber cleans. Several suppliers manufacture or integrate remote plasma systems for retrofits to existing process tools to replace in situ PFC cleans.

• Pros

- Commercially available technology from several suppliers that reduce chamber clean PFC emissions by 99%.
- Significantly reduced PFC emissions from CVD chamber cleans.

- Remote cleans result in improved tool utilization through reduced clean times, reduced wet clean frequency, improved mean time between failures (MTBF), reduced chamber parts costs. Additionally, they improve yield through reduced defects and decrease COO.
- CVD tools not equipped with remote cleans may be retrofitted with remote cleans.
- Cons
 - Implementing NF_3 remote cleans results in generation of much greater F_2 and HF emissions than fluorocarbon-based cleans, and requires additional treatment to remove these gases from the exhaust stream.
 - Point-of-use (POU) abatement may be necessary in fabs where house scrubber infrastructure is not sufficient to abate the HF/F₂ generated.
 - Coated stainless steel ductwork may be required.
 - Little information is publicly available on retrofits to non-Applied Materials tools.

• Typical Remote Plasma Required Utilities

Argon, NF₃, or other PFC, electricity, process cooling water (PCW), toxic gas monitoring for NF₃.

• Reported Results

PFC Utilization Efficiency (%)		% PFC Emissions Reduction From Baseline Process
NF ₃	>95–99	>15–99
C ₃ F ₈	>95	>35

• Byproducts

Remote cleans converts NF_3 and other PFC into F+ ions and radicals. Units generate significant emissions of F_2 and HF that must be abated. When using NF_3 to clean carbon-containing low-k chambers, a small amount of CF_4 is generated. No information is available on byproducts when using PFCs other than NF_3 as input gas.

• Cost

Contact suppliers for cost information.

Remote Plasma Unit Manufacturers or Integration Specialists

- New Power Plasma Co., Ltd. produces remote high-density plasma generators that decompose NF₃ or C₃F₈ for CVD chamber cleaning. <u>http://newpower.co.kr</u>.
- MKS Instruments, Inc. produces the ASTRON family of integrated remote plasma sources with flow rates of 2.0 slm up to 15 slm for semiconductor and flat panel CVD chamber cleaning. In addition to NF₃, ASTRON hf-s series generators can dissociate alternative PFC gases such as C₂F₆, C₃F₈, CF₄, or SF₆. <u>http://www.mksinst.com/</u> <u>PRG1.html</u>.

 LegacyTek offers a remote clean retrofit integration package to Applied Materials P5000 DxL and Centura DxZ 200 mm chambers; they are currently seeking beta partners to integrate remote cleans on Novellus tools. The LegacyTek upgrade package includes an MKS Instruments Astron or Astron-I remote plasma unit, integration package, installation and process startup. <u>http://legacytek.com/index.htm</u>.

• Recent Publications

- L. Mendicino, P. T. Brown, S. Filipiak, C. Nauert, H. Estep, M. Fletcher, A. Atherton, and T. Nowak, "Fab Impacts of Implementation of Remote Clean for CVD Chamber Clean," *Proceedings of the SEMICON Southwest – A Partnership for PFC Emissions Reduction Workshop*, oral paper #6 (2001).
- W. Worth, "Evaluation of Applied Material's Remote Clean Technology for Chamber Cleans and its Impact on a Fab's Wastewater Treatment Facilities," *Proceedings of the 8th ISESH Conference*, paper 20.3C.3, ECSv2002-15, p. 127, 2001.
- S. Bailey, M. Goulding, L. Tousignant, L. Zazzera, and S. Shao, "Evaluation of an MKS ASTRONex and C₃F₈ for Remote Plasma Chamber Clean," *Proceedings of the SEMICON West 2002 STS Symposium*, session 104, paper #2, 2002.

ECS v2002-15, p. 144.

G. Loh, Y. Osaki, and M. Mocella, "Remote Plasma Chamber Cleaning with the MKS ASTRONex Unit," *Proceedings of the 11th ISESH Conference*, PFC paper #4, 2004.

• References

Information on remote cleans provided by Laura Mendicino of Freescale, Wang-Keun Kim of Samsung, and Chris Lewis of LegacyTek. Additional information obtained from websites of New Power Plasma Co. and MKS Instruments, Inc.

A.4 Alternative Chemistry

Alternative chemistry, or chemical substitution, is the use of chemicals with lower global warming potential (GWP) or no GWP as alternatives to PFCs. Alternative chemistry also includes high GWP gases that are more efficiently used in plasma processes, resulting in an overall greenhouse gas emissions reduction.

Technology Status

In research and development and commercially available.

- Pros
 - Alternative chemistries reduce total PFC emissions.
 - Drop-in chamber clean alternatives can be implemented with little to no additional cost and do not require additional ESH measures to be installed.
 - Alternative chemistries may also provide process benefits.
 - Implementing alternative chemistries can result in decreased gas consumption and improved COO.

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- Cons
 - Implementing an alternative chemistry may require process re-qualification, especially for etch processes where the wafer is affected.
 - Certain alternatives increase ESH risk and require additional engineering controls.

A.4.1 Chamber Clean Alternatives

a) Hexafluoroethane (C₂F₆) for PECVD Chamber Cleans

 CF_4 was the original POR for cleaning certain 150 mm PECVD process chambers. CF_4 utilization efficiency in chamber cleans is reported as 0.2. One semiconductor company has reported replacing CF_4 with hexafluoroethane (C_2F_6), resulting in a >57% emissions reduction due to decreased input gas consumption and more efficient PFC utilization.

• Applicability and Status

 \leq 150 mm and 200 mm CVD chamber clean. Commercially available and currently in use.

• Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of gas input (%) (mass/mass)	% PFC Emissions Reduction from Baseline C ₂ F ₆ Process
C_2F_6	17–24	11–13 (CF ₄)	>57

• Cost

No cost to implement unless process re-qualification required.

- Pros
 - Significantly reduced PFC emissions from CVD chamber cleans.
- Cons
 - May require process re-qualification.
 - Other alternative chemistries may results in greater PFC emissions reductions.

Recent Publications

N/A

References

Information received from an SIA member company.

b) Octofluoropropane (C₃F₈) for PECVD Chamber Cleans

 C_2F_6 was the original POR used to clean the majority of 150 mm and early 200 mm PECVD process chambers. Industry members are using octofluoropropane (C_3F_8) as an alternative to C_2F_6 . C_3F_8 has a higher destruction removal efficiency (DRE) compared to C_2F_6 that can result in decreased gas consumption and emissions. Recent process optimization has resulted in decreased CF₄ byproduct by optimizing the C_3F_8/O_2 ratio.

• Applicability and Status

 \leq 150 mm and 200 mm CVD chamber cleans. Commercially available and currently in use as a retrofit in manufacturing fabs. Novellus has developed C₃F₈ chamber clean PORs for Novellus Concept One and Concept Two SiN, SiON, SiO, and TEOS processes.

Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
C ₃ F ₈	30–60	12–30 (CF ₄)	12–70

• Cost

No cost to implement unless process re-qualification required. Process results in a decreased COO of 20–65%.

• Pros

- No capital cost drop-in replacement.
- Equivalent clean times.
- Reduced PFC emissions from CVD chamber cleans.
- Reduced COO.
- Cons
 - May require process requalification.
 - Can result in significant CF₄ byproducts.
 - Other alternative chemistries may result in greater PFC emission reductions.

• Recent Publications

S. Kesari, T. Bach, L. Tousignant, W. Reagen, and L. Zazzera, "Process Optimization and PFC Emission Reduction Using C₃F₈ Chamber Clean Processes in Applied Materials P-5000 PECVD Tools," 2nd International Symposium on Environmental Issues with Materials and Processes for Electronics and Semiconductor Industries, *Electrochem. Soc. Proceedings*, L. Mendicino, Editor, 1999.

• References

Information received from SIA member companies including Bronwyn Pierce of HP.

c) Octofluorocyclobutane (c-C₄F₈) for PECVD Chamber Cleans

c-C₄F₈ is being used to replace C_2F_6 and other fluorocarbon chamber clean chemistries. c-C₄F₈ dissociates more clean gas when compared to C_2F_6 and certain other fluorocarbon chemistries. Clean process uses more O_2 , but reduces CF₄ formation.

• Applicability and Status

 \leq 150 mm and 200 mm CVD chamber clean. Commercially available and currently in use as a retrofit in manufacturing fabs.

Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
c-C ₄ F ₈	70–90	4–11 (CF ₄)	50–85

• Cost

No/low cost to implement unless process re-qualification required. Existing perfluorocarbon gas line can be used; mass flow controller (MFC) size may need to be reduced due to much lower $c-C_4F_8$ gas flow.

- Pros
 - Drop-in replacement resulting in reduced PECVD chamber clean PFC emissions.
 - 20–75% decrease in COO due to decreased gas requirements.
- Cons
 - May require process re-qualification.
 - Generates CF₄ byproduct.
 - Other alternatives may result in greater PFC emission reductions.

• Recent Publications

- E.M. Chan, G. Loh, and C.C. Allgood, "Process Optimization and Perfluorocompound (PFC) Emission Reduction Using a c-C4F8 Chamber Cleaning Process on a Novellus Concept 1 Dielectric Plasma Enhanced Chemical Vapor Deposition (PECVD) Tool," IEEE Transactions on Semiconductor Manufacturing, **17**, p.497, 2004.
- K. Avala, L. Liu, D. Brindza, G. Loh, and S.A. Moiyadi, "<u>Reduced Perfluorocompound</u> (PFC) Emissions and Gas Consumption Using a c-C4F8-based Plasma Enhanced Chemical Vapor Deposition (PECVD) Chamber Clean Chemistry," *IEEE Transactions on Semiconductor Manufacturing*, **17**, p.504, 2004.
- C. Allgood, M. Mocella, H. Chae, and H. Sawin, "<u>Evaluation of Octafluorocyclobutane</u> as a Chamber Clean Gas in a Silicon Dioxide Plasma Enhanced Chemical Vapor <u>Deposition (PECVD) Reactor</u>," *J. Electrochem. Soc.*, **150**, G122, 2003.

- C.H. Oh, N.-E. Lee, J.H. Kim, G.Y. Yeom, S.S. Yoon, and T.K. Kwon, "Effect of N-containing Additive Gases on Global Warming Gas Emission During Remote Plasma Cleaning Process of Silicon Nitride Plasma Enhanced Chemical Vapor Deposition (PECVD) Chamber Using C4F8/O2/Ar Chemistry," Surface and Coatings Technology, **171**, p.267, 2003.
- A. Evans, L. Nevala, M. Sledz, and C.C. Allgood, "Advances in Reducing Perfluorocompound (PFC) Emissions and Gas Costs: Qualification of c-C₄F₈ Chamber Clean in a Novellus Concept-2 Chemical Vapor Deposition (CVD) Tool," *Proceedings of the 9th International Semiconductor ESH Conference*, PFC Session A, Paper #1, 2002.
- A. Evans, L. Nevala, and C. Allgood, "Advances in Reducing Perfluorocompound (PFC) Emissions and Gas Costs: Qualification and Implementation of c-C₄F₈ Chamber Clean Gas in a Novellus Concept-2 Chemical Vapor Deposition (CVD) Tool," *Proceedings of the SEMICON Southwest PFC Seminar*, Session 3, Paper 3, 2002.

• References

Information received from an SIA member company, Francesca Illuzzi of STMicroelectronics, and Gary Loh of DuPont.

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d) Octafluorotetrahydrofuran (C₄F₈O) for PECVD Chamber Cleans

 C_4F_8O is currently being used to replace perfluorocarbons such as C_2F_6 and C_3F_8 in PECVD chamber cleans. C_4F_8O is an alternative chamber clean chemistry with higher DRE, resulting in reduced gas consumption. Higher DRE and reduced consumption lead to reduced PFC emissions and lower COO.

• Applicability and Status

 \leq 150 mm and 200 mm CVD chamber clean. Commercially available and currently in use as a retrofit in manufacturing fabs.

• Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
C ₄ F ₈ O	85–90	10–20 (CF ₄) 4 (C ₃ F ₈)	70–90

• Cost

No cost to implement unless process re-qualification required. Special attention is required for monitoring corrosion effects of reactor parts. Weight monitoring is recommended for cylinder fill information. Low-pressure regulators at gas cabinet are recommended.

- Pros
 - Drop-in replacement with significantly reduced PFC emissions from CVD chamber cleans.
 - 20–50% reduction in COO.
- Cons
 - May require process re-qualification.
 - Monitoring of parts for corrosion effects is necessary.
 - Generates CF₄ byproduct, although at a lower rate than some alternatives.

• Recent Publications

- K.J. Kim, C.H. Oh, N.-E. Lee, J.H. Kim, J.W. Bae, G.Y. Yeom, and S.S. Yoon, "Global Warming Gas Emission During Plasma Cleaning Process of Silicon Nitride Using c-C₄F₈O Feed Gas with Additive N₂," *Han'guk Pyomyon Konghak Hoechi*, **34**, 403, 2001; *Chem. Abstr.*, **138**, 94335, 2003.
- C.H. Oh, N.-E. Lee, J.H. Kim, G.Y. Yeom, S.S. Yoon, and T.K. Kwon, "Increase in Cleaning Rate and Reduction in Global Warming Effect During C₄F₈O/O₂ Remote Plasma Cleaning of Silicon Nitride by Adding NO and N₂O," *Thin Solid Films*, 435, 264, 2003.
- D. Harman, J. Flood, and E. Frendberg, "Evaluation of C₄F₈O as an Alternative Material in Chemical Vapor Deposition (CVD) Chamber Cleaning," *Proceedings of the 9th International Semiconductor ESH Conference*, PFC Session A, Paper #4, 2002.
- D. Harman, J. Flood, and E. Frendberg, "Evaluation of C₄F₈O for Chemical Vapor Deposition (CVD) Chamber Cleans," *Proceedings of the SEMICON West 2002 STS Symposium*, Session 104, Paper #3, 2002.
- J.H. Kim, J.W. Bae, C.H. Oh, K.J. Kim, N.E. Lee, and G.Y. Yeom, "C₄F₈O/O₂/N-based Additive Gases for Silicon Nitride Plasma Enhanced Chemical Vapor Deposition (PECVD) Chamber Cleaning with Low Global Warming Potentials," *Jpn. J. Appl. Phys.*, 41, p. 6570, 2002.
- R. Van San, S. Kesari, and L. Zazzera, "Evaluation and Qualification of C₄F₈O as an in situ Cleaning Gas for Plasma Enhanced Chemical Vapor Deposition (PECVD) Tools," SEMI Conference Proceedings – A Partnership for PFC Emission Reduction, SEMICON Southwest, October 2000.

• References

Information received from Harry Thewissen of Philips Semiconductor, Francesca Illuzzi of STMicroelectronics, and an SIA member company.

e) Nitrogen Trifluoride (NF₃) for in situ PECVD Chamber Cleans

 NF_3 is currently being used in manufacturing fabs as a replacement for in situ perfluorocarbon PECVD chamber cleans. Additionally, Novellus is using dilute in situ NF_3 cleans for their advanced 200 mm and 300 mm tools. NF_3 has a high DRE when used in plasma; moreover, unlike fluorocarbons, NF_3 does not generate CF_4 byproduct unless it is used to clean carbon-containing films. When compared to C_2F_6 , NF_3 cleans require less clean gas and result in faster clean times.

• Applicability and Status

Commercially available and currently in use as a retrofit for ≤ 150 mm and 200 mm CVD chamber clean. POR on advanced 200 mm and 300 mm Novellus tools. NF₃ is also used for thin film transistor liquid crystal display chamber cleans.

Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
NF ₃	60–80	0–4 (CF ₄) Depending on carbon content of film removed	20–90

• Cost

Toxic gas monitoring and additional safety measures may be necessary. Upgraded exhaust duct and point-of-use fluorine abatement may be needed.

• Pros

- Significantly reduced PFC emissions from CVD chamber cleans.
- Unlike fluorocarbons, NF₃ does not generate CF₄ byproduct unless it is used to clean carbon-containing films.

• Cons

- In situ NF₃ is not a drop-in replacement; NF₃ is an oxidizer and has a lower LD50 than C₂F₆.
- Toxic gas monitoring may be necessary.
- Clean process may result in higher emissions of HF and F₂ as well as NO_x.
- ESH controls such as local scrubbing may be required; additionally, one semiconductor manufacturer recommended installation of coated stainless steel exhaust duct.
- Monitoring of parts for corrosion effects is necessary.
- May require process requalification.

References

Information received from SIA member companies.

f) Carbonyl Fluoride (COF₂) for PECVD Chamber Cleans

 COF_2 is a toxic gas with low GWP and no ozone depletion potential. From 1998–2002, Japan's Research Institute of Innovation Technology for the Earth undertook an effort to identify alternative chamber clean chemistries, eventually recommending COF_2 as a replacement gas. With a GWP of 1, COF_2 has a much lower global warming potential than PFCs used for chamber cleans. Although COF_2 is toxic, it is easily removed from the exhaust stream by water scrubbing. When used in plasma, a small amount of CF_4 byproduct is produced. Recent efforts in Japan have focused on evaluating COF_2 in manufacturing applications.

• Applicability

 \leq 150 mm and 200 mm CVD chamber clean. Currently undergoing evaluation in manufacturing fabs in Japan.

• Reported Results

At the 12th ISESH Conference held in 2005, Japan Electronics and Information Technologies Industries Association members presented results of COF_2 evaluations as alternatives to C_2F_6 and C_3F_8 cleans in manufacturing environments. On a 200 mm Novellus Concept Two running PETEOS. Panasonic reports that COF_2 cleans resulted in a 96% PFC emission reduction and equivalent cleaning performance when compared to C_2F_6 with no adverse affect to the tool. On a Novellus Concept One depositing silicon nitride film on eighty thousand 125 mm and 150 mm bipolar wafers, Sanyo reported a 97% PFC emission reduction and no technical difficulties when compared to the baseline C_3F_8 process. CF_4 byproduct was between 1.2–1.8%.

• Cost

Although not listed in conference proceedings, a gas cost of 20,000Yen/kg was mentioned at the 12th Annual ISESH Conference. Additional ESH controls are required. Incompatibilities may require re-piping process gases into the chamber. POU scrubbing may be required.

- Pros
 - 96–97% reduction in PE-CVD chamber clean PFC emissions.
 - Faster clean times.
- Cons
 - High gas cost.
 - Additional ESH controls required.
 - Sanyo notes that, because reactivity with NH₃ is high, separate gas lines into the chamber must be installed to prevent inadvertent mixing.
 - May require process requalification.

• References

- M. Sakamura, T. Minegishi, and M. Yomoda, "Evaluation of COF₂ in Mass Production Line," *12th Annual ISESH Conference*, June, 2005.
- S. Ueda, K. Takahashi, T. Matsubara, and H. Nikou, "Investigation of an Alternative Gas COF₂ Application for Chemical Vapor Deposition (CVD) Chamber Cleaning Process," *12th Annual ISESH Conference*, June, 2005.
- Y. Mitsui, "Alternative Gas for Chemical Vapor Deposition (CVD) Cleaning COF₂," *12th Annual ISESH Conference*, June, 2005.

g) Fluorine (F₂) for CVD Chamber Cleaning

 F_2 has been discussed as a possible alternative to PFCs for CVD chamber cleaning but had been discarded as a serious alternative in the past due to the ESH risks associated with transport, storage, and use of high-pressure F_2 cylinders. BOC-Edwards and Fluorine on Call, Ltd. have each developed onsite fluorine generators that convert anhydrous HF into F_2 by electrolysis. After the F_2 is generated, it is purified to remove residual HF and other contaminants. It can then be fed into PECVD chambers for plasma-enhanced in situ cleans. Samsung reports evaluating in situ generated F_2 to replace NF₃ for low-pressure chemical vapor deposition (LPCVD) or CVD chamber cleaning on 300 mm tools. This evaluation is in the research and development stage.

• Applicability

 \leq 150 mm, 200 mm, 300 mm and thin film transistor liquid crystal display CVD chamber cleans. Processes are currently in R&D.

• Cost

Contact suppliers for cost of on site F_2 generators. Although additional engineering controls are required, Samsung anticipates that replacing NF₃ with onsite generated fluorine will result in 20% cost savings due to reduced chemical and operational costs.

- Pros
 - While anhydrous HF is toxic and corrosive and F₂ is highly toxic and a strong oxidizer, neither of these gases are global warming gases.
 - No PFC emissions will be generated during CVD chamber cleans unless F₂ is used to remove carbon-containing films.
- Cons
 - Fluorine generation and use poses additional ESH risks that must be addressed when designing installation site, piping, and generator system.
 - POU abatement may be required to abate F₂ emissions from chamber clean.

• Recent Publications

S. Siegele, D. Hage, and F. Siegele, "<u>On-Site Generation of High Purity Fluorine (F2)</u> as a Safe and Economical Alternative for Chemical Vapor Deposition (CVD) <u>Chamber Cleaning</u>," *FutureFab International*, Issue 13, July, 2002.

Generation-F 80 Onsite Fluorine Generator, BOC-Edwards Product Data Sheet.

• References

Information received from Wang-Kim Keun of Samsung, Chris Case of BOC-Edwards, and Dan Hage of Fluorine on Call, Ltd.

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Dan Hage <u>dhage@focltd.com</u> 512-329-8866

A.4.2 Alternative Etch Chemistries

While replacement of high GWP gases with lower or non-GWP gases is generally preferable, it has not proven feasible in most plasma etch applications. Processing requirements for high aspect ratio plasma etching continue to become more stringent, requiring both fluorine to etch and the right carbon to fluorine ratio to ensure anisotropic etching. A significant amount or research has been done on alternative etchants such as iodofluorocarbons, hydrofluorocarbons, and unsaturated fluorocarbons; however, many of these chemicals are not viable alternative etchants in a manufacturing environment due to excess polymerization, lack of etch selectivity, difficulties in delivering gases to the process chamber, and potential increased employee exposure risks.

One alternative that is being implemented in manufacturing is C_4F_6 , which is being used as a dielectric etch gas for advanced ULSI integration, replacing CF_4 , CHF_3 , and C_4F_8 .

• Applicability

 C_4F_6 is being used in advanced 200 mm and 300 mm manufacturing fabs for oxide and low-k etching where high selectivity for silicon is required in the presence of nitride or other films with high aspect ratios, thinner resists and less etch resistant resists.

• Reported Results

Replacement Chemistry	Utilization Efficiency (%)	PFC Byproduct Generation as % of Gas Input (%) (mass/mass)	% PFC Emissions Reduction From Baseline C ₂ F ₆ Process
C_4F_6	> 95	5–10 (CF ₄)	>90 in some cases

• Pros

- C_4F_6 is a process enabling technology for CD control and etch selectivity and, with an atmospheric lifetime <1 year and utilization efficiency >95%, PFC emission reductions >90% can be achieved.

 C₄F₆ can be implemented as an alternative chemistry using existing hardware and gas lines; however, toxic gas monitoring may be needed.

• Cons

- As is the case with all higher molecular weight fluorocarbon compounds used in plasma processes, some CF₄ byproduct is formed and emitted.

• Recent Publications

- S. Karecki, L. Pruette, R. Reif, T. Sparks, L. Beu, and V. Vartanian, "Use of Novel <u>Hydrofluorocarbon and Iodofluorocarbon Chemistries for a High Aspect Ratio Via Etch</u> <u>in a High Density Plasma Etch Tool</u>," *Journal of the Electrochemical Society*, Vol. 145, No. 12, December 1998.
- S. Karecki, R. Chatterjee, L. Pruette, R. Reif, T. Sparks, L. Beu, and V. Vartanian, "Evaluation of Pentafluoroethane and 1,1-Difluoroethane for a Dielectric Etch <u>Application in a High Density Plasma Etch Tool</u>," *Jpn. J. Appl. Phys.*, 39, Part 1 (7B), 4666–4686, July 2000.
- R. Chatterjee, S. Karecki, R. Reif, T. Sparks, V. Vartanian, B. Goolsby, "Evaluation of <u>Hexafluorobenzene as an Environmentally Benign Dielectric Etch Chemistry</u>," *Journal of The Electrochemical Society*, Volume 148, Issue 12, pp. G721–G724, December 2001.
- F. Fracassi, R. d'Agostino, E. Fornelli, F. Illuzzi, and T. Shirafuji, "<u>SiO2 Etching with</u> <u>Perfluorobutadiene in a Dual Frequency Plasma Reactor</u>," *Journal of Vacuum Science & Technology* A: Vacuum, Surfaces, and Films, Volume 21, Issue 3, pp. 638–642, May 2003.
- A.D. Johnson, R.G. Ridgeway, and P.J. Maroulis, "<u>Reduction of Perfluorocompound (PFC)</u> <u>Emissions to the Environment Through Advances in Chemical Vapor Deposition (CVD)</u> <u>and Etch Processes</u>," *IEEE Transactions on Semiconductor Manufacturing*, 17, p. 491, November 2004.

• References

Information on C_4F_6 was provided by Ajay Somani of MIT, Laura Mendicino and Victor Vartanian of Freescale Semiconductor, and Robert Ridgeway of Air Products and Chemicals, Inc.

Robert Ridgeway ridgewrg@airproducts.com 610-481-4436

A.5 Capture/Recovery

A.5.1 Air Liquide PFC Capture and Recycle

In 2003, Air Liquide installed a compact membrane capture and recirculation system for SF₆ at a power IC manufacturer. The IC manufacturer uses SF₆ as a blanket gas during IC testing. A mixture of 60% SF₆ and 40% air is exhausted from the testers. The Air Liquide unit compresses the exhaust stream, which is then fed into two membrane separation units. Because the SF₆ is being used as a blanket gas, not as a plasma etchant, byproducts requiring pre-treatment are not present in the exhaust stream. Air Liquide reports an 89% SF₆ recovery rate at >99% purity. Recovered SF₆ is fed back into the testers.

• Project Status

System is in operation and Air Liquide reported in 2004 that the system had paid for itself in related cost savings.

• Applicability

The Air Liquide membrane separation system has a modular design for a wide range of PFC flow rates. It appears to be most cost effective when used for specialized, single PFC, high volume processes. The lack of plasma and other process byproducts in this particular application makes capture-recovery relatively straightforward and cost effective.

• Pros

- Cost effective and environmentally preferred method for addressing emissions from clean, high volume, single PFC processes.

• Cons

 Centralized PFC capture/recovery has not been implemented in semiconductor manufacturing because it has been deemed too costly to implement due to pretreatment requirements and decreasing PFC concentrations over time in the exhaust.

• References

C-H Ly, R. Daniel, and C. Anderson, "Perfluorocompound (PFC) Emission Reduction Via Membrane Capture Processing in Semiconductor," *11th Annual ISESH Conference*, 2004.

A.6 Abatement

A.6.1 PFC Abatement – POU Fueled Burner – Scrubber Units

General Technology Description

Point-of-use fueled burner-scrubber units use a propane, methane, natural gas or hydrogen flame to destroy PFCs and other hazardous substances such as deposition precursors followed by a water scrubber, which may contain a base solution, to remove volatile acid gases from the exhaust stream. Burner-scrubber units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of nitrogen (from pump purge and ballast) that can lower the combustion unit temperature, thus, typically requiring the addition of oxygen to the reach flame temperatures high enough to destroy the carbon based PFCs and SF_6 . Burner-scrubber units can typically abate emissions from multiple process chambers.

• Applicability

Both CVD and etch effluents from \leq 150 mm, 200 mm, and 300 mm process tools can be treated with the burner-scrubber units.

• Pros

- Commercially available from multiple suppliers
- Technology that abates both etch and CVD chamber clean PFC emissions at ≥95% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
- Fueled systems destroy F₂, converting it into HF, and scrub the HF byproduct.
- Units are capable of abating emissions from multiple process chambers.
- Largest installed base of abatement systems in the industry.

• Cons

- Requires H₂ or natural gas (NG) fuel. Generates HF liquid waste stream which may require further treatment before discharge.
- May generate NO_x.
- To be used as a retrofit in an existing fab requires floor space, which may be limited, and either H_2 or NG, which may not be installed as a service utility.
- Manufacturers of Burner-Scrubber Units Without Detailed Information in this Appendix
 - ATTO Co, Ltd., produces modified Centrotherm abatement devices for the Korean market. <u>http://atto.co.kr/2004e/product/pro_012_04.htm</u>
 - Global Standard Technology Co., Ltd., company produces modified DAS abatement systems for the Korean market. <u>http://www.gst-in.com/contents/business/product/</u> <u>product01/0111.asp</u>
 - UNI-SEM, Korean manufacturer of UN2000-A thermal oxidizer with wet scrubber using H2 as fuel. The footprint is 750 mm × 870 mm × 2262 mm. <u>http://uni-sem.com/</u> <u>html/pfcmain.html</u>

a) BOC Edwards Thermal Processor Unit (TPU)

• Description

The TPU is a point-of-use abatement device, installed post-vacuum pump, which utilizes an inwardly fired combustor followed by a three-stage wet scrubber and using proprietary combustion methods to ensure maximum DRE of PFCs and process gases. The TPU operates in two modes: high fire and low fire. In high fire mode, higher flows of fuel and O_2 are injected to abate PFCs (with communication between process equipment and the TPU). The footprint is 1300 mm × 625 mm × 1833 mm. Addition of

the scrubber water recirculation unit (WRU) increases width to ~1600 mm. The unit is installed downstream of the vacuum pumps and can handle effluent from multiple chambers (up to four) with a maximum flow capacity of 200 slm.

• Technology Status

Commercially available.

• Applicability

Both CVD and etch effluents can be treated with the TPU. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Electricity, water (~6 gpm), natural gas, N_2 , O_2 , acid waste drain, acid scrubbed exhaust, and general exhaust. Scrubber water consumption can be reduced to <1 gpm makeup water by installing the WRU. The WRU requires cooling water.

DRE (%) * PFC ۸ Maximum PFC Input Flow Rate (sccm) # NF_3 6000# > 95 99.99 99 SF_6 12000# 90 to > 905 99.9 95 2500-10000* / 6400# 85 to > 95 99.9 95 C_2F_6 6000# CHF₃ 90 99.99 99 C₄F₈ 6000# 95 99.9 99 6400# C_3F_8 99.9 99.9 95 2000* / 6000# CF₄ 90-96 93 90 3300 mg/m³ * CH_2F_2 > 95* 900 mg/m³ * C_5F_8 > 90*

• Reported Results

* Performance reported by semiconductor manufacturers

Supplier reported performance

^ Supplier guaranteed

• Byproducts

Byproducts of combustion for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. NO_x is emitted at ~75 ppm/inlet while destroying CF_4 due to high operating temperature. NF₃ combustion results in formation of N₂, HF, and NO_x. One semiconductor manufacturer reports CO emissions at ~50 mg/m³.

• Cost of Technology (provided by supplier)

\$120,000 USD per unit.

• Cost of Ownership

TPU requires replacement of seals, gaskets, and combustor (depends on process) as needed for annual PM. Consumable costs are variable and can range from ~\$4000–\$8000 USD annually. One semiconductor company noted high cost to operate mainly due to heavy maintenance and consumables. Typical annual facilities costs for operation of the TPU based on *Fab Utility Cost Values for Cost of Ownership (COO) Calculations* (SEMATECH, Technology Transfer #02034260A-TR) is ~\$8000 USD.

- Pros
 - Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥93% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
 - Destroys F₂ and removes the resulting HF.
 - Unit is capable of abating emissions from multiple process chambers.
 - Established technology with installed base of TPUs in multiple semiconductor facilities in the U.S., Europe, and Asia.
- Cons
 - Requires NG, which may not be available as a service utility.
 - Generates HF liquid waste stream, which may require further treatment before discharge.
 - Abatement of CF₄ and NF₃ generates NO_x.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited, and NG, which may not be installed as a service utility.
 - Oxygen, which also may not be available as a service utility, or compressed dry air (CDA) may be necessary to abate CF₄.
- Contact

Joe Van Gompel 512-633-5105 joe.vangompel@bocedwards.com

• References

Information on the TPU was provided by SIA and ISMI member companies including Bronwyn Pierce of HP, a member of ESIA, and Francesca Illuzzi of STMicroelectronics, and by Joe Van Gompel of BOC-Edwards.

b) BOC Edwards Mini-TPU

• Description

The Mini-TPU is a point-of-use abatement device, installed post-vacuum pump, which utilizes an inwardly fired combustor followed by a three-stage wet scrubber and using proprietary combustion methods to ensure maximum DRE of PFCs and process gases. It is designed strictly to abate emissions from oxide etch and poly etch processes only and is not suitable for CVD. Maximum exhaust flow rate through the Mini-TPU is 50 slm. The mini-TPU is not sold as a standalone unit but is incorporated with high efficiency vacuum pumps in a package called Zenith Etch that is designed for cost- and space-effective PFC abatement. The total footprint of abatement and pumps is 1300 mm $\times 625 \text{ mm} \times 1833 \text{ mm}.$

• Technology Status

Commercially available.

• Applicability

Oxide and poly etch effluents can be treated with the Mini-TPU. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Electricity, water, NG, N₂, O₂, acid waste drain, acid scrubbed exhaust, and general exhaust.

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
NF ₃	1000	>99
SF ₆	1000	>99
C_4F_8	1000	>99
CH_2F_2	1000	>99
C_4F_6	1000	>99
C₅F ₈	1000	>99
CF ₄	1000	93

• Supplier Reported Results

• Byproducts

Byproducts of combustion for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. NO_x is negligible for all other PFCs except NF₃, which realizes about 20% conversion to NO_x of NF₃ that actually makes it out of the process chamber and into the abatement device.

• Cost of Technology (provided by supplier)

Capital cost as low as \$30,000 USD per inlet on etch processes.

• Cost of Ownership

TPU requires replacement of seals, gaskets, and combustor (depends on process) as needed for annual PM. Consumable costs are typically <\$4000 USD annually. Typical annual facilities costs for operation of the Mini-TPU based on *Fab Utility Cost Values for Cost of Ownership (COO) Calculations* (SEMATECH, Technology Transfer #02034260A-TR) is ~\$4000 USD.

- Pros
 - Commercially available technology that abates oxide and poly etch emissions at \geq 93% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream. It also destroys F₂ and removes the resulting HF.
 - Unit is capable of abating emissions from multiple process chambers.
- Cons
 - Requires NG, which may not be available as a service utility.
 - Generates HF liquid waste stream, which may require further treatment before discharge.
 - Abatement of NF₃ generates NO_x.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited; and NG, which may not be installed as a service utility.
 - May require oxygen or compressed dray air (CDA) to abate CF₄, which may not be available as a service utility.

• Contact

Joe Van Gompel 512-633-5105 joe.vangompel@bocedwards.com

• References

Information on the mini-TPU was provided by Joe Van Gompel of BOC Edwards.

c) Centrotherm CT-BW Burner Washer

• Description

Centrotherm has developed a modular abatement system whose components can be specified based on the specific requirements of the process being abated. The Centrotherm CT-BW contains a cone-shaped burner chamber and a separate high efficiency wet scrubber section. The CT-BW is sold as a single system or a 100% redundancy dual system. The footprint ranges from 650 mm × 800 mm × 1850 mm to 800 mm × 1300 mm × 2000 mm. The unit can handle effluent from multiple chambers with a maximum flow rate of 600 slm.

Technology Status

Commercially available.

• Applicability

Both CVD and etch effluents can be treated with the CT-BW. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Electricity, cooling water (~7 slm), O₂, NG, or hydrogen, scrubber water (1.5 slm makeup water), KOH, or NaOH for scrubber.

• Supplier Reported Results (no semiconductor manufacturer provided data available)

PFC	Maximum PFC Input Flow Rate (sccm) DRE (%)		
NF ₃	10,000	99	
SF ₆	7000	99	
C_2F_6	7000	99	
CHF₃		99	
C_4F_8		99	
CF ₄	7000	84–95	

• Byproducts

Byproducts of combustion for carbon-containing PFCs include CO_2 and HF. Final rinse from scrubber contains KF or NaF. NF₃ combustion results in formation of N₂, HF, and NO_x. Final scrubber rinse contains KF, KNO₂, and KNO₃. NO_x formation depends on set up of the system and flow of N₂ vs. the set-up of the flame.

• Cost of Technology (provided by supplier)

\$95,000-\$110,000 USD per unit.

• Cost of Ownership

No information provided.

- Pros
 - Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥95% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
 - Unit is capable of abating emissions from multiple process chambers.
 - Modular design with 100% redundancy capability.
 - Newer burner-washer technology than CT-FLM with installed base of CT-BWs in semiconductor facilities in Europe and Korea.
 - Centrotherm's Asia partner is ATTO, which sells a modified device adapted to the Korean market.

- Cons
 - Requires H₂ or NG.
 - Generates HF liquid waste stream which may require further treatment before discharge; however, Centrotherm has developed an HF treatment system.
 - May generate NO_x.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited, and either H_2 or NG, which may not be installed as a service utility.
- Contact

Volker Kinzig Volker.Kinzig@centrotherm.de Phone 0049-7344-918-1801

References

Information provided by Volker Kinzig of Centrotherm.

d) Centrotherm FLM (CT-FLM) Flawamat Burner-Scrubber

• Description

The CT-FLM is a point-of-use abatement device, installed post-vacuum pump, in which effluent enters an inner tube where it is burned. Effluent from the burner chamber leaves the bottom of the burner through an outer tube where it is washed from the top by a spray nozzle. The CT-FLM is sold as a single system. The footprint is from $650 \text{ mm} \times 800 \text{ mm} \times 1850 \text{ mm}$. The unit is installed downstream of the vacuum pumps and can handle effluent from multiple chambers with a maximum flow capacity of 300 slm.

• Technology Status

Commercially available.

• Applicability

Both CVD and etch effluents can be treated with the CT-FLM. Tool can be installed as a retrofit or during new tool installation.

• Required Utilities

Electricity, water, oxygen, NG or hydrogen, KOH- or NaOH-solution for scrubber, HF waste drain.

Reported Results

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
NF ₃		> 95–99
SF ₆	3000#	> 95* / 99#
C_2F_6	3000#	> 90–98*
CHF ₃		98*
C_4F_8		99*
C_3F_8		98*
CF ₄	3000#	90–95*

*Performance reported by semiconductor manufacturer(s) # Supplier reported performance

• Byproducts

Byproducts of combustion for carbon-containing PFCs include CO_2 and HF. Final rinse from scrubber contains KF or NaF. NF₃ combustion results in formation of N₂, HF, and NO_x. Final scrubber rinse contains KF, KNO₂, and KNO₃. NO_x formation depends on set up of the system and flow of N₂ vs. the set-up of the flame.

• Cost of Technology (provided by supplier)

\$95,000-\$110,000 USD per unit.

• Cost of Ownership

FLM requires regular cleaning of internal parts, resulting in periodic cleaning costs and maintenance effort.

- Pros
 - Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥95% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
 - Unit is capable of abating emissions from multiple process chambers.
 - Established technology with installed base of CT-FLMs in multiple semiconductor facilities in Europe and Korea.
 - Centrotherm's Asia partner is ATTO, which sells a modified device adapted to the Korean market.

• Cons

- Requires H₂ or NG.
- Generates HF liquid waste stream which may require further treatment before discharge; however, Centrotherm has developed an HF treatment system.
- May generate NO_x.
- To be used as a retrofit in an existing fab requires floor space, which may be limited, and either H_2 or NG, which may not be installed as a service utility.

• Contact

Volker Kinzig Volker.Kinzig@centrotherm.de Phone 0049-7344-918-1801

References

Information on the FLM was provided by Gabriele Fetzer of Philips Semiconductor, Wang-Keun Kim of Samsung, Francesca Illuzzi of STMicroelectronics, and Volker Kinzig of Centrotherm.

e) DAS ESCAPE-INLINE

• Description

The ESCAPE INLINE is a point-of-use abatement device, installed post-vacuum pump, in which effluent from up to four process chambers enters a combustion chamber. Toxic, flammable, or pyrophoric compounds as well as PFCs are decomposed in the flame by pyrolysis, reduction and oxidation reactions. Directly after the combustion chamber the gas is quenched rapidly and passed through a wet scrubber column where acidic compounds and particulate matter are retained. The scrubber liquid is recirculated and automatically exchanged without interruption of the abatement process. The footprint is 688 mm × 830 mm × 2070 mm (standard version) and has a maximum flow capacity of 200 slm.

• Technology Status

Commercially available with >1200 units installed.

• Applicability

Both CVD and etch effluents can be treated with the ESCAPE-INLINE. Abatement device can be installed as a retrofit or during new tool installation.

• Required Utilities

NG, LPG, or hydrogen for fuel; electricity, water, oxygen, CDA, cooling water, N_2 . KOH- or NaOH-solution for scrubber, HF waste drain.

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)	
NF ₃	6000#	> 95*	99#
SF ₆	3000#	> 95*	95#
C_2F_6	3000#	> 90*	95#
CHF₃	6000#		99#
CH_2F_2	10,000#		99#
C_3F_8	2500#		99#
CF_4	5000#	90*	95#

• Reported Results

*Performance reported by semiconductor manufacturer(s)

Supplier reported performance

• Byproducts

Byproducts of combustion for carbon-containing PFCs include CO_2 and HF. According to supplier, NO_x levels are lower than required by national clean air standards (specific country and standards not cited).

• Cost of Technology (per unit)

Not provided. Contact supplier to obtain a quote.

• Cost of Ownership

Consumables are required for proper operation and maintenance but specific information not available.

• Pros

- Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥95% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
- Unit is capable of abating emissions from multiple process chambers.
- Established technology with installed base in multiple semiconductor facilities.
- Cons
 - Requires fuel.
 - Generates HF liquid waste stream, which may require further treatment before discharge.
 - May generate NO_x.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited, and either H₂, LPG, or NG, which may not be installed as a service utility.

• Contact

Dr. A. Frenzel <u>frenzel@das-europe.de</u> Phone 49-351-871 8634

• References

Information provided by Francesca Illuzzi of STMicroelectronics and A. Frenzel of DAS.

S-N Li, et al, "FTIR Spectrometers Measure Scrubber Efficiencies," *Solid State Technology*, July 2002.

f) Ecosys Marathon 8500

• Description

The Ecosys Marathon 8500 is a point-of-use abatement device, installed post-vacuum pump, which utilizes a staged natural gas or liquid propane gas combustor followed by a wet scrubber to ensure maximum DRE of PFCs and process gases. The footprint is 1168 mm \times 637 mm \times 2261 mm. The unit is installed downstream of the vacuum pumps and can handle effluent from multiple process chambers and tools with a maximum flow capacity of 700 slm.

• Technology Status

Commercially available.

• Applicability

Both CVD and etch effluents can be treated with the Marathon 8500. Device can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

208/220 VAC; 10 A, 2 kW; 0.3–1.25 gpm fresh water; 2–15 gpm cooling water; 70 scfm CDA; 35 scfm N_2 ; 1.3–3.5 scfm natural gas, acid waste drain, 120 scfm exhaust.

• Supplier Reported Results (no semiconductor manufacturer provided data available)

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
NF ₃	4500	99
SF ₆	5000	99
C_2F_6	> 2400 (not tested at higher flow)	> 99.9
C_3F_8	> 3000 (not test at higher flow)	> 99.9
CF4	8000	97
CF ₄	4000	98
CF_4	2000	99

• Byproducts

Byproducts of combustion for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. CO and NO_x production is below 500 lbs/year/device.

• Cost of Technology (provided by supplier)

\$ 120,000 USD per unit.

• Cost of Ownership

Ecosys indicates cost of parts and labor on an annual basis to be \$3700 and COO on an annual basis is \$5300.

- Pros
 - Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥97% DRE and removes HF, generated as a result of burning PFCs, from the exhaust stream.
 - Unit is capable of abating emissions from multiple process chambers and multiple tools.

• Cons

- Requires NG or LPG, which may not be available as a service utility.
- Generates HF liquid waste stream, which may require further treatment before discharge.
- Abatement generates CO and NO_x; the ESH impact of these needs to be assessed.
- To be used as a retrofit in an existing fab requires floor space, which may be limited, and NG or LPG, which may not be installed as a service utility.

• Contact

Sebastien Raoux, Ecosys 408-719-4668 Sebastien_Raoux@metrontech.com

• References

Information on the Ecosys Marathon 8500 was provided by Sebastien Raoux of Ecosys.

A.6.2 PFC Abatement – POU Catalytic–Scrubber Units

• General Technology Description

Point-of-use catalytic-scrubber units use a catalyst to promote the destruction of PFCs and process gases at lower activation energies than would otherwise be needed. Catalytic systems operate at a lower temperature than other PFC abatement systems and do not require fuel. A water scrubber typically follows the catalytic reactor to remove HF byproduct from the exhaust stream. Catalytic-scrubber units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of nitrogen. Catalytic-scrubber units can typically abate emissions from multiple process chambers.

• Applicability

Both CVD and etch effluents from \leq 150 mm, 200 mm, and 300 mm process tools can be treated with the burner-scrubber units.

- Pros
 - Catalytic-scrubber units operate at lower temperatures than other PFC abatement systems and do not utilize a fueled flame.

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• Cons

- Pre-scrubbers are required to prevent catalyst poisoning.
- Catalyst has a limited lifetime and must be replaced periodically.
- Cost of ownership needs to be evaluated.

a) Ecosys Trinity

• Description

The Ecosys Trinity is a point-of-use abatement device, installed post-vacuum pump, which uses state of the art catalytic methods to ensure maximum DRE of PFCs and process gases. The etch exhaust stream first passes through a water scrubber where water soluble gases and particles are removed, then into the catalytic reactor where PFCs are reacted to form HF, and finally through a second water scrubber to remove the HF. The Trinity has a 686 mm \times 914 mm \times 2006 mm footprint and can handle multiple chambers with an flow capacity of 200 slm.

• Technology Status

Commercially available.

• Applicability

The Trinity can abate etch emissions. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities:

Water, air, electricity, acid waste drain, process gas exhaust.

• Supplier Reported Results

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
C ₃ F ₈	1000	99

* Maximum flow indicated is for C₃F₈, which is the most challenging PFC for a catalytic-based abatement device. Greater PFC flows and/or DREs can be obtained for other PFC gases and mixtures. Please contact Ecosys for more details.

• Byproducts

By products for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber.

• Cost of Technology (provided by supplier)

\$100,000 USD per unit.

• Cost of Ownership

Catalyst must be replaced periodically; lifetime >1 year.

- Pros
 - Commercially available technology that abates etch PFC emissions at 99% DRE and removes HF, generated as a result of catalyzing PFCs, from the exhaust stream.
 - Lower operating temperature than burner-scrubber units and no open flame.

• Cons

- Limited applicability.
- Pre-scrubber required to prevent catalyst poisoning.
- To be used as a retrofit in an existing fab requires floor space, which may be limited.

• Contact

Brian Kingston brian.kingston@metrontech.com Phone 408-887-6132

References

robin.gardiner@metrontech.com

"EM Trinity Local Scrubber Efficiency Evaluation," ITRI Taiwan, April 2004.

"Catalytic Technology for Perfluorocompound (PFC) Emissions Control," Solid State Technology, July 2001.

R.S. Brown and J.A. Rossin, "<u>Catalytic Process for Control of Perfluorocompound</u> (PFC) Emissions, Semiconductor International, June 2001.

b) Hitachi Super Catalytic Decomposition System (SCDS)

• Description

The Hitachi Super Catalytic Decomposition System (SCDS) is a point-of-use abatement device, installed post-vacuum pump, which uses state of the art catalytic methods to ensure maximum DRE of PFCs and process gases. The SCDS is available in 60, 120, or 200 slm capacities. Each SCDS consists of a pre-spray and packed bed scrubber to remove particulates and water soluble acids, catalytic reactor and cooling section, and post-reactor packed bed scrubber to remove HF from the exhaust stream. The SCDS uses recirculated wastewater for each of the scrubber units, thus minimizing the amount of fresh water required.

Technology Status

Commercially available.

• Applicability

The SCDS can abate CVD and etch emissions. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

Model	CD-60	CD-120	CD-200
Capacity (slm)	60	120	200
Electrical (kW)	4	8	11
Water Usage (gpm)	0.4	0.6	0.9
System Size (W \times D \times H) (mm)	$991 \times 559 \times 1880$	$1143\times 635\times 1880$	$1143\times 635\times 1880$

Reported Results

		DRE (%)	
PFC	Maximum PFC Input Flow Rate (sccm)	*	#
NF ₃		NT	99.9
SF ₆		NT	99.9
C_2F_6	1100	> 99	99.9
CHF₃	2400	> 99	99.9
C_4F_8		NT	99.9
C_3F_8	80	> 99	99.5
CF_4	7400	> 99	93
C₅F ₈		NT	99.9

* Performance reported by semiconductor manufacturer for CD-120. # Supplier reported performance from website.

• Byproducts

Byproducts for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. The fate of the N from NF₃ is not described.

• Cost of Technology (per unit)

Not provided. Contact the supplier to obtain a quote.

• Cost of Ownership

Hitachi website states that catalyst replacement is required every 12–24 months; the pre-packed tower and pre-spray, cooling room and wastewater tank require annual cleaning; the packed tower requires cleaning every 2 years. According to a user, various parts are required for quarterly, semi-annual, annual or "as needed" maintenance.

- Pros
 - Commercially available technology that abates both etch and CVD chamber clean PFC emissions at ≥99% DRE and removes HF, generated as a result of catalyzing PFCs, from the exhaust stream.
 - Recirculating scrubber results in low water consumption.
 - SCDS comes in three sizes and is capable of abating emissions from multiple process chambers.
 - Established technology.

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- Cons
 - To be used as a retrofit in an existing fab requires floor space, which may be limited.
 - Cost of ownership needs to be evaluated.

References

Hitachi America did not respond to requests for additional information submitted by the web and email. SCDS specifications were obtained from: <u>http://www.hitachi-hta.com</u>.

Information on the SCDS was provided by Joachim Stache of Philips.

c) TecHarmonic EHTVS/Alpine S

• Description

The TecHarmonic EHTVS/Alpine S catalytic scrubber is a comprehensive point-of-use abatement device for particulates, acid gases, flammables and PFCs. The Alpine S utilizes a high temperature, electrically heated thermal oxidizer chamber to preheat the exhaust stream, followed by a vortex particulate scrubber and packed bed tower which connects to a catalytic chamber to destroy PFCs, followed by a second vortex particulate scrubber and packed bed tower. Scrubber water re-circulation is used to minimize the amount of fresh water required by the system. The Alpine S is installed post-vacuum pump and can handle effluent from multiple process chambers and tools with a maximum flow capacity of 300 slm. The footprint is 965 mm \times 1194 mm \times 1918 mm.

Technology Status

Commercially available and installed in a PFC abatement application on an Applied Materials Centura 4 chamber SiN/TEOS deposition tool.

• Applicability

The Alpine S can abate CVD and etch emissions. The Alpine S is suited to handling all PFCs. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Water (1.5 gpm scrubber makeup water), N₂, CDA, electricity, acid waste drain, cabinet exhaust, acid process exhaust.

		DRE (%)	
PFC	Maximum PFC Input Flow Rate (sccm)	*	#
NF ₃	10,000#	> 95	90–99
SF ₆	6000#	> 95	90–99
C_2F_6	6000#	> 95	90–99
C ₃ F ₈	6000#		90–99
CF ₄	6000#	90	90–99
C_4F_8	6000#		90–99
CHF ₃	6000#		90–99

• Reported Results from Manufacturing Installations

*Performance reported by semiconductor manufacturer(s) #Supplier reported performance from manufacturing installations

• Byproducts

Byproducts for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. Supplier reports that no NO_x emissions are formed.

• Cost of Technology (per unit)

Not provided. Contact supplier to obtain a quote.

• Cost of Ownership

Periodic replacement of thermocouples and catalyst required. Frequency not reported. TecHarmonic estimates annual cost to operate the Alpine P to be ~\$17,000-\$20,000 in PFC abatement applications.

• Pros

- Commercially available technology that abates particulates, acid gases, flammables and PFC emissions from etch and CVD chamber clean.
- PFC DREs are 90–99% and device removes HF, generated as a result of PFCs destruction, from the exhaust stream.
- Recirculating scrubber results in low water consumption.
- Alpine S is capable of abating emissions from multiple process chambers.
- The Alpine S has >1 year experience abating PFC from production.
- Cons
 - To be used as a retrofit in an existing fab requires floor space, which may be limited.
 - Cost data must be obtained from supplier.
 - Limited performance data from semiconductor manufacturers.

• Contact

Bill Delaney bdelaney@techarmonic.com Phone 408-360-8780, x201

• References

Information on the Alpine S was provided by Francesca Illuzzi of STMicroelectronics and Bill Delaney of TecHarmonic.

A.6.3 PFC Abatement – POU Electrically Heated Thermal – Scrubber Units

• General Technology Description

POU electrically heated thermal-scrubber units use an electrically heated chamber to destroy PFCs and other hazardous substances such as deposition precursors, followed by a water scrubber to remove volatile acid gases from the exhaust stream. Electrically heated thermal-scrubber units are installed on the process tool exhaust line after the vacuum pump. Electrically heated-scrubber units can typically abate emissions from multiple process chambers.

• Applicability

Both CVD and etch effluents from \leq 150 mm, 200 mm, and 300 mm process tools can be treated with the burner-scrubber units.

- Pros
 - If >90% efficiency is obtained for all PFCs, total GHG emissions should be lower with this technology compared to burner-scrubbers.
 - By using electricity to heat the unit, a flammable fuel and open flame are not required which reduces potential fire risks for the fab.
 - Operating costs should be lower than burner-scrubber units, assuming units have high MTBF and low maintenance requirements.
- Cons
 - High temperatures are required to abate CF₄, a known byproduct of any plasma process using fluorocarbons or used to etch or clean carbon-based films.
 - Many electrically heated thermal-scrubber units cannot abate CF₄.
- Manufacturers of Electrically Heated-Scrubber Units Without Detailed Information in this Appendix

Centrotherm CT-EW: As part of their modular abatement system design, Centrotherm is developing an electrically heated burner to abate pyrophoric deposition gases, NF₃, and SF₆. The unit has 600 slm capacity and uses CDA as the oxidation gas instead of O₂. For more information on alpha and beta test results and commercial availability, contact Volker Kinzig, <u>Volker.Kinzig@centrotherm.de</u>, Phone 0049-7344-918-1801.

a) TecHarmonic EHTVS/Alpine P

• Description

The TecHarmonic EHTVS/Alpine P is a comprehensive point-of-use abatement device for particulates, acid gases, flammables and certain PFCs using dual high temperature, electrically heated thermal oxidizers followed by vortex particulate scrubber and twin packed bed towers. Scrubber water re-circulation is used to minimize the amount of fresh water required by the system. The Alpine P is installed post-vacuum pump and can handle effluent from multiple process chambers and tools with a maximum flow capacity of 800 slm. The footprint is 965 mm \times 1194 mm \times 1918 mm.

• Technology Status

Commercially available and installed in PFC abatement applications for >3 years.

• Applicability

The Alpine P can abate CVD and etch PFC emissions, but is most effective at abating SF₆ and NF₃. The Alpine S is better suited to handling carbon-containing PFC exhaust streams. Tool can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Supplier Reported Results from Manufacturing Installations

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
NF ₃	20,000	95–99
SF ₆	6000	95–99
C ₂ F ₆ *	6000	85–99
C ₃ F ₈ *	6000	85–99

* CF₄ is a plasma process byproduct; CF₄ abatement efficiency is not reported.

• Byproducts

Byproducts for carbon-containing PFCs are CO_2 and HF. HF is removed in the wet scrubber. Supplier reports that no NO_x emissions are formed.

• Cost of Technology (per unit)

Not provided. Contact supplier to obtain a quote.

• Cost of Ownership

Periodic replacement of thermocouples and gaskets is required. Frequency not reported. TecHarmonic estimates annual cost to operate the Alpine P to be ~\$5000.

• Pros

- Commercially available technology that abates certain PFC emissions from etch and CVD chamber clean at 85–95% DRE and removes HF, generated as a result of PFCs, from the exhaust stream.
- Recirculating scrubber results in low water consumption.

- Alpine P is capable of abating emissions from multiple process chambers.
- Established technology.
- Cons
 - DRE for CF₄ was not provided.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited.
 - Cost data must be obtained from supplier.
 - No user data provided by semiconductor manufacturers.

• Contact

Bill Delaney bdelaney@techarmonic.com Phone 408-360-8780, x201

• References

Information on the Alpine P was provided by Bill Delaney of TecHarmonic.

b) Kanken Techno KT1000 Series

• Description

Kanken Techno has developed the KT line of electrically heated thermal destruction units with pre-and post-scrubbers for comprehensive point-of-use abatement of particulates, acid gases, flammables and PFCs. The inlet scrubber removes hydrolytic effluents from the process such as SiF_4 and WF_6 and provides water to react with PFCs in the electric heater reactor. Kanken Techno has five different heater chamber designs which operate at different temperatures or exhaust flow rates. Selection of a particular system is dependent on the anticipated process emissions. The post-scrubber removes HF generated from PFC destruction and particulate. Scrubber water re-circulation is used to minimize the amount of fresh water required by the system. The KT1000 is installed post-vacuum pump and can handle effluent from multiple process chambers and tools.

• Technology Status

Commercially available with multiple installations in PFC abatement applications.

• Applicability

Tool can be installed as a retrofit or during new tool installation on ≤ 150 mm, 200 mm, and 300 mm process tools. See table below for applicability of specific systems.

Model		KT100MF	KT1000F	KT1000H	KT1000EX	
Applicability		NF ₃ CVD Chamber Cleans	NF ₃ CVD Chamber Cleans	Etch and CVD	Etch	
Total Capacity (slm)		400	250	200–250	120 for CF_4 200 for SF_6	
Dimensions	Single Port	1100 × 1050 × 1900	1050 × 1100 ×	1100 × 1350 ×	1100 × 1050 ×	
(mm)	Multi Port	1100 × 1350 × 1900	1900	1900	1900	
Electrical		35	35	35	35	
(kVA)	Avg.	7	7	7	7	
Water Usage (Ipm)		10	10	10	10	
Process Gas (s	Process Gas (slm)		NH3: 6	N/A	N/A	
Exhaust (slm)		1000	500	500	500	
Acid Waste Dra	ain (Ipm)	10	10	10	10	
	Electric Heater	1/2 yr	1/2 yr	1/2 yr	1/2 yr	
Consumables	Shower Nozzle	1/yr	1/yr	1/yr	1/yr	
	Recycle Water Pump	1/yr	1/yr	1/yr	1/yr	

• Required Utilities and Consumables

• Supplier Reported Results from Manufacturing Installations: KT1000MF

PFC	PFC Maximum PFC Input Flow Rate (sccm)	
NF ₃	15000	> 99%*

*< TLV: 10 ppm.

• Supplier Reported Results from Manufacturing Installations: KT1000F

PFC	Maximum PFC Input Flow Rate (sccm) DRE (
NF ₃	6000	> 99%*

*< TLV: 10 ppm.

• Supplier Reported Results from Manufacturing Installations: KT1000H

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
C_4F_8	7500	> 90
C ₃ F ₈ *	7500	> 90
C ₂ F ₆ *	6000	> 90
CHF ₃ *	7500	> 90

* CF₄ is a plasma process byproduct for this input chemistry; CF₄ abatement efficiency is 16.6%.

PFC	Maximum PFC Input Flow Rate (sccm) DRE (%	
CF ₄	3600	> 90
SF ₆	6000	> 90

• Supplier Reported Results from Manufacturing Installations: KT1000EX

• Byproducts

Generates HF byproduct. HF is removed in the wet scrubber. KT1000EX generates SO_x emissions, which are removed by a wet scrubber. Supplier reports that no NO_x emissions are formed. KT1000MF and KT1000F introduce NH_3 as a reactant gas to prevent the formation of NO_x during NF_3 abatement.

• Cost of Technology (per unit)

Not provided. Contact supplier to obtain a quote.

• Cost of Ownership

Operating costs not provided. Required consumables and replacement frequency reported above.

- Pros
 - Commercially available technology that abates PFC emissions from specified applications at >90%DRE and removes HF, generated as a result of PFC destruction, from the exhaust stream.
 - Recirculating scrubber results in low water consumption.
 - Capable of abating emissions from multiple process chambers.
 - Commercially available, established technology with large installed base.
- Cons
 - CF_4 is a byproduct of plasma processes using C-F chemistries; KT1000EX is only KT unit capable of abating $CF_4 > 90\%$ DRE.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited.
 - Cost data must be obtained from supplier.
 - No data provided by semiconductor manufacturers.

• Contact

Tatsuro Beppu 81-6-6380-1474 mailto:beppu@kanken-techno.co.jp

• References

Information on the KT1000 Series was provided by Tatsuro Beppu of Kanken-Techno.

A.6.4 PFC Abatement – POU Atmospheric Plasma Units

• General Technology Description

Point-of-use atmospheric plasma units use plasma at atmospheric pressure to destroy PFCs and other hazardous substances such as deposition precursors. The plasma reactor can be followed by a water scrubber, which may contain a base solution, to remove volatile acid gases from the exhaust stream. Atmospheric plasma units are installed on the process tool exhaust line after the vacuum pump and, thus, the exhaust stream entering the unit contains a large amount of nitrogen, which can impact the plasma efficacy. Atmospheric plasma units are typically designed to abate emissions from multiple process chambers.

• Technology Status

Commercially available.

• Applicability

Emissions from \leq 150 mm, 200 mm, and 300 mm process tools can be treated.

• Pros

- By using plasma, a flammable fuel and open flame are not required which reduces potential fire risks for the fab.
- Operating costs should be lower than burner-scrubber units, assuming units have high MTBF and low maintenance requirements.
- Using post-pump plasma minimizes the risk of fluorine or HF formation in the vacuum pump that could lead to pump corrosion.
- Unlike pre-pump plasma systems, post-pump plasma units pose no risk of particulates diffusing back into the process chamber.
- Cons
 - POU atmospheric plasma units are a relatively new and unproven technology.
 - Little data is currently available on DRE, uptime, maintenance requirements, and COO.

a) Air Liquide UPAS

• Description

Air Liquide has developed an atmospheric microwave plasma system/dry adsorption system. Integration of universal plasma abatement system (UPAS) technology into a fab may require installation of pretreatment technology and will require post-UPAS abatement to remove HF from the exhaust stream. Centralized wet scrubbers installed for acid exhaust may be adequate. Air Liquide makes two versions of the UPAS. The Compact UPAS is 635 mm × 700 mm × 1900 mm while the Integrated UPAS is 635 mm × 1300 mm × 1900 mm. The UPAS can handle effluent from multiple process chambers with maximum flow of 120 slm.

Technology Status

Commercially available with 14 units currently installed in manufacturing fabs.

• Applicability

UPAS is marketed for etch process emissions; however, a paper was presented at ISESH 2005 on application to CVD chamber cleans. Device can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Electricity, N₂, CDA, cooling water, acid exhaust, process heat exhaust.

• Reported Results

PFC	Maximum PFC Input Flow Rate (mg/m ³)	DRE (%)
C_4F_8	6700	> 99
CF ₄	7300	> 90
CH_2F_2	500	> 99
CHF₃	6700	> 95

• Byproducts

ESIA member notes NO_x is generated at $\sim 250 \text{ mg/m}^3$.

• Cost of Technology (per unit)

Not provided. Contact supplier to obtain a quote.

• Cost of Ownership

Air Liquide notes periodic replacement of ceramic tube (2 tubes as backup), cooling oil (120L), gaskets and other parts may be required. Frequency not reported. ESIA member notes dry cartridges as a consumable.

- Pros
 - PFC and fluorinated species abatement with reduced corrosion and safety risk in main exhaust.
 - Potentially lower operating cost than fueled burner-scrubber units; however, technology is relatively new and little information is publicly available on uptime and COO.

• Cons

- Limited applicability.
- May require installation of separate pretreatment system to remove particulates and acid gases.
- Does not remove HF or other acids generated in plasma; semiconductor manufacturers must determine if central wet scrubbers can sufficiently abate additional UPAS effluent.
- NO_x is generated by the plasma system (cracking of O₂ and N₂) and is not treated by dry cartridge.
- Solid deposition in the cartridge is NO_x-based.

Technology Transfer #05104693A-ENG

• Contact

Olivier Letessier <u>olivier.letessier@airliquide.com</u> Phone +33 1 40 62 5234

• References

Information provided by ESIA members and Olivier Letessier of Air Liquide.

- H. Yamamoto (Ricoh Electronics Devices), "Perfluorocompound (PFC) Atmospheric Plasma Abatement for Etch and Chemical Vapor Deposition (CVD)," *ISESH*, 2004.
- H. Yamamoto (Ricoh Electronics Devices), M. Tabata (Air Liquide Japan Tokyo, Japan), M. Sato and C-H. Ly (Air Liquide Laboratories, Ibaraki, Japan), and J.C. Rostaing (Centre de Recherche Claude Delorme, Les-Loges-en-Josas, France), "Perfluorocompound (PFC) Atmospheric Plasma Abatement System for Chemical Vapor Deposition (CVD) at Ricoh: A Pertinent Approach," *ISESH*, 2005.

b) BOC Edwards Zenith Etch Plasma

• Description

BOC Edwards offers the Zenith Etch Plasma, an atmospheric microwave plasma unit followed by a three-stage wet scrubber incorporated with high-efficiency vacuum pumps for plasma etch chambers. The Zenith Etch Plasma system is not a standalone abatement device; four vacuum pumps are included. The footprint is 1300 mm \times 625 mm \times 1833 mm, which includes the abatement system and pumps.

Technology Status

Zenith Etch Plasma is commercially available only in Europe at this time.

• Applicability

Zenith Etch Plasma system is available as a retrofit or as part of a new tool installation for etch systems only.

• Required Utilities

Water, electricity, N₂, O₂, PCW, acid exhaust, general exhaust.

• Supplier Reported Results

PFC	Maximum PFC Input Flow Rate (sccm)	DRE (%)
NF ₃	1000	> 99
SF ₆	1000	> 99
C_4F_6	1000	> 99
C_4F_8	1000	> 99
CF ₄	800	91
CH_2F_2	1000	> 99
CH ₃	1000	> 99

• Byproducts

All PFCs are converted to CO_2 and HF. BOC Edwards reports HF is removed by a wet scrubber, and NO_x emissions are within desired levels.

• Cost of Technology (provided by supplier)

As a package including abatement and 4 vacuum pumps, the Zenith Etch system is between \$50,000–\$75,000 USD per etch chamber depending on the configuration (all piping between pumps and abatement included).

• Cost of Ownership

BOC Edwards lists as consumables electrode, seals, gaskets as needed for annual PM. BOC Edwards reports consumables costs are typically <\$3000 USD and typical facilities costs based on <u>Fab Utility Cost Values for Cost of Ownership (COO)</u> <u>Calculations</u> (SEMATECH, Technology Transfer #02034260A-TR), the fab utility cost values are ~\$4000 USD.

• Pros

Potentially lower operating cost than fueled burner-scrubber units; however, technology is relatively new and little information is publicly available on uptime and COO.

• Cons

Limited applicability and availability.

• Contact

Joe Van Gompel joe.vangompel@bocedwards.com Phone 512-633-5105

• References

M. Radiou, A. Seeley, S. Carss, and J. Van Gompel, "Sixty Percent Utilities Savings on Etch Perfluorocompound (PFC) Abatement," *SEMICON West*, July 2003.

c) Centrotherm Plasma-Washer

• Description

Centrotherm has developed a modular point-of-use abatement system whose components can be specified based on the specific requirements of the process being abated. The Centrotherm plasma-washer combines a microwave plasma stage and a separate high efficiency wet scrubber section. Dry bed absorber or catalysts are alternatives to the wet scrubber section. The unit is installed after the vacuum pump and operates at atmospheric pressure. The footprint is dependent on system configuration. The unit can handle effluent from multiple chambers with a maximum flow capacity of 120 slm.

Technology Status

Alpha and beta testing.

• Applicability

Centrotherm's plasma-washer can be installed as part of a new etch tool installation or as a retrofit for etch processes; CVD is problematic due to powder generation.

• Required Utilities

Electricity, water or oxygen as reactant, nitrogen; scrubber water, KOH or NaOH for scrubber.

• Supplier Reported Results (no semiconductor manufacturer provided data available)

PFC	Maximum PFC Input Flow Rate (sccm) DRE (%)		
SF ₆	2000	80–90*	
C_2F_6	2000	80–90*	
CF ₄	2000	80–90*	

*Depending on set-up.

• Byproducts

No information provided on byproducts.

• Cost of Technology (provided by supplier)

\$115,000-\$130,000 USD per unit.

• Cost of Ownership

Electrodes for the plasma tube must be replaced periodically (contact supplier to obtain additional information).

- Pros
 - By using plasma, a flammable fuel and open flame are not required which reduces potential fire risks for the fab.
 - Operating costs should be lower than burner-scrubber units, assuming units have high MTBF and low maintenance requirements.
 - Using post-pump plasma minimizes the risk of fluorine or HF formation in the vacuum pump that could lead to pump corrosion.
 - Unlike pre-pump plasma systems, post-pump plasma units pose no risk of particulate back diffusion into the process chamber.
- Cons
 - Relatively new and unproven technology with limited applicability.
 - Little data available on DRE, uptime, maintenance requirements, and COO; however, it is not recommended for CVD due to particulates and polymeric buildup in the plasma tube.
 - To be used as a retrofit in an existing fab requires floor space, which may be limited.

• Contact

Volker Kinzig Volker.Kinzig@centrotherm.de Phone 0049-7344-918-1801

References

Semiconductor contacts are MUT Jena and Innovent (Jena, Germany).

Information provided by Volker Kinzig of Centrotherm.

d) Desiccant Technology Corporation (D-Tech) Plasma + Wet Scrubber Model LT-DP200VI

• Description

D-Tech has developed an integrated atmospheric plasma and wet scrubber system to abate PFC and chlorofluorocarbon emissions from etch and CVD processes. The unit also destroys CVD precursors and treats SiF_4 byproducts. The unit is 1200 mm \times 1000 mm \times 1850 mm and can handle effluent from multiple chambers with a maximum flow capacity of 600 slm.

• Technology Status

Commercially available.

• Applicability

Plasma + Wet Scrubber can be used to abate both etch and CVD emissions. Device can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm process tools.

• Required Utilities

Electricity (220 V, 40 A, 50/60 Hz), N₂ (45 lpm @ 5 kg/cm²), CDA (30 lpm @ 3– 5 kg/cm²), cooling water (40 lpm @ 3–5 kg/cm²), city water (2.5 lpm @ 3 kg/cm²).

• Supplier Reported Results (no semiconductor manufacturer provided data available)

PFC	Maximum PFC Input Flow Rate (sccm) DRE (%)	
CF ₄	250	> 99
C_2F_6	4000	> 99
CHF₃	1000	> 99

• Byproducts

HF is formed.

• Cost of Ownership

D-Tech reports replacement of torch (1 each/40 days), thermocouple (5 each/year), and O-ring seal (8 each/6 months).

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- Pros
 - Potentially lower operating cost than fueled burner-scrubber units; however, technology is relatively new and little information is publicly available on uptime and COO.
- Cons
 - May require installation of separate pretreatment system to remove particulate and acid gases.
 - Does not remove HF or other acids generated in plasma; semiconductor manufacturers must determine if central wet scrubbers can sufficiently abate additional UPAS effluent.

• Contact

Art Liu art@dtech.com.tw Phone +886-3-5832511

• References

Information provided by Art Liu of D-Tech.

A.6.5 PFC Abatement – POU Foreline Plasma Units

• General Technology Description

POU foreline plasma units employ a compact, low-pressure plasma reactor to destroy PFCs from etch processes. Foreline plasma units are installed on the foreline after the turbo pump but before the mechanical vacuum pump, where they can abate concentrated emissions before dilution with N_2 purge from the vacuum pump. One unit is required per etch process chamber.

• Technology Status

Commercially available.

• Applicability

Device can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm etch process chambers.

- Pros
 - Compact footprint and potentially lower COO solution to abate etch PFC emissions.
- Cons
 - Does not remove HF or other acid gases generated in plasma that are then fed into the vacuum pump.

- Semiconductor manufacturers must monitor impact of acid gases on vacuum system and determine if central wet scrubbers have sufficient capacity to abate additional acid gases generated by the pre-pump plasma units.
- In certain applications, pre-pump plasma units pose a potential risk of particles diffusing back into the etch process chamber.

a) Advanced Energy (AE) PCS (successor to Litmas Blue)

• Description

The PCS is a high density, inductively coupled plasma generator that is installed on the foreline between the turbo and mechanical vacuum pumps of an etch chamber to decompose unused PFCs into ions and free radicals as they enter the vacuum pump. Water vapor is added to ensure conversion to HF. Placement of the PCS in the foreline results in energy-efficient decomposition of PFC emissions when they are most concentrated (i.e., before dilution with nitrogen purge from the vacuum pump). The PCS operates so that the plasma is ON when PFC gases flow in the process chamber and OFF when the chamber is idle. AE has partnered with CS Clean Systems to sell and service the AE line of PFC abatement products, including the PCS. AE makes 1500 W and 3000 W models of the PCS. Footprint of both units is $398 \times 274 \times 264$ mm.

• Technology Status

Commercially available with multiple units currently installed in manufacturing fabs.

• Applicability

The PCS is applicable to etch processes. Device can be installed as a retrofit or during new tool installation on ≤ 150 mm, 200 mm, and 300 mm process tools. One unit is required per etch process chamber.

• Required Utilities

Water, electricity.

Reported Results

PFC	Maximum PFC Input Flow Rate (ppm) DRE (%)	
CHF ₃	700	>> 95
CF ₄	850	> 90

• Byproducts

HF, NO₂, and COF_2 at low ppm level.

• Cost of Technology (per unit)

Not reported. Contact CS Clean Systems.

• Cost of Ownership

Plasma tube requires periodic replacement. 5% increase in COO.

- Pros
 - Potentially lower COO solution to abate etch PFC emissions because PFCs are treated before dilution by pump purge nitrogen.

• Cons

- Does not remove HF or other acid gases generated in plasma that then feed into the vacuum pump.
- Semiconductor manufacturers must monitor impact of acid gases on vacuum system and determine if central wet scrubbers have sufficient capacity to abate additional acid gases generated by the PCS.
- CS Clean Systems makes CLEANSORB dry absorber system to remove HF.

• Contact

Contact CS Systems for additional information.

• References

Information provided by Ton van de Kerkhof of Philips. Additional information obtained from the CS Clean Systems. <u>http://www.cscleansystems.com/index.asp</u>.

b) Ecosys Barracuda

• Description

The Ecosys Barracuda is a low-pressure plasma reactor that is installed on the foreline between the turbo and mechanical vacuum pumps of an etch chamber. Placement of the Barracuda in the foreline results in energy-efficient decomposition of PFC emissions when they are most concentrated (i.e., before dilution with nitrogen purge from the vacuum pump). The plasma is ON when PFC gases flow in the process chamber and OFF when the chamber is idle. Plasma power can be adjusted to achieve appropriate DRE, depending on the PFC gas mixture and flow rate. To ensure PFC byproducts are not formed, Barracuda utilizes water vapor as a reactant. Reactor size is $45.7 \times 25.4 \times 25.4 \text{ cm}$. Dimensions of the controller, which can be located remotely, are $38.1 \times 25.4 \times 20.3 \text{ cm}$.

Technology Status

Currently undergoing beta testing.

• Applicability

Ecosys Barracuda is being developed to abate etch process emissions. Device can be installed as a retrofit or during new tool installation on \leq 150 mm, 200 mm, and 300 mm etch process tools. One unit is required per process chamber.

• Required Utilities

Water, electricity.

• Reported Results

		DRE (%)	
PFC	Maximum PFC Input Flow Rate	*	#
CHF ₃	850 ppm*	>> 95	
CF ₄	700 ppm* / 120 sccm#	> 90	90

* Performance reported by semiconductor manufacturer

Supplier reported performance – maximum flow indicated is for CF₄, which is most challenging PFC to abate. Greater flows and DREs can be obtained for other PFCs and gas mixtures. Contact Ecosys for more details.

• Byproducts

HF, COF₂, NO₂, CO, and CO₂.

• Cost of Technology (provided by supplier)

Target price: \$30,000 USD per unit.

• Cost of Ownership

Ceramic plasma tube requires periodic replacement (lifetime estimated to be >1 year).

Pros

- Small footprint and potentially lower COO solution for abating etch PFC emissions.
- Cons
 - Because unit is undergoing beta testing, little information is available about longterm reliability and COO.
 - Does not remove HF or other acid gases generated in plasma that then feed into the vacuum pump.
 - Semiconductor manufacturers must monitor impact of acid gases on vacuum system and determine if central wet scrubbers have sufficient capacity to abate additional acid gases generated by the Barracuda.
 - If necessary, dry bed absorber system or wet scrubber can also be installed postpump to abate HF.

• Contact

Sebastien Raoux, Ecosys 408-719-4668 Sebastien_Raoux@metrontech.com

• References

Information on the Ecosys Barracuda was provided by Ton van de Kerkhof of Philips and Sebastien Raoux of Ecosys.

A.6.6 PFC Abatement – Centralized Atmospheric Plasma Unit

• General Technology Description

The only centralized PFC abatement system is a corona discharge system jointly developed by FH Co., Ltd and Samsung Electronics in Korea. The technology is undergoing beta evaluation by Samsung. At the beta site, a separate PFC exhaust is installed post-vacuum pump to segregate CVD chamber clean emissions from deposition emissions. The PFC exhaust passes through the annular space between co-axial cylindrical electrodes used to sustain a corona discharge at atmospheric pressure. Exhaust from the abatement system then flows to the house scrubber for removal of acid gases. The unit has a capacity of 50 cubic meters/minute and dimensions of $1500 \times 3330 \times 1731$ mm. Multiple units can be installed to provide required capacity. Deposition process exhaust goes to separate flammable duct.

Technology Status

Extensive beta testing (20+ months). Multiple units installed in fabs in Korea.

• Applicability

PFC emissions from semiconductor and LCD display CVD chamber cleans.

- Pros
 - Centralized abatement for CVD chamber clean PFC emissions.
 - Modular design allows for installation of multiple units to achieve required flow capacity.

• Cons

- New technology with limited installations.
- Little detailed information available on DRE, maintenance requirements, COO, reliability, and uptime.
- Requirement of separate exhaust system for PFCs may make use of this technology as a retrofit difficult due to space limitations in existing fabs.

• Required Utilities

Power consumption is 220 V, 6 A.

Reported Results

PFC	Maximum PFC Input Flow Rate (ppm)	DRE (%)
NF ₃	65	91.2
C ₃ F ₈	110	90.1

• Byproducts

Not reported. Exhaust flows to central wet scrubbers.

• Cost of Technology (provided by supplier)

\$500,000 USD per unit.

• Contact

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• References

S-K Chae, "New Large-Scale End-of-Pipe Perfluorocompound (PFC) Abatement System Using a High-Efficiency Atmospheric Discharge Technology," *SEMICON West 2004*, STS:ISM Program, July 2004.

Additional information provided by Wang-Keun Kim of Samsung.

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