Tool Perfluorocompound (PFC) Emissions Data Report

SEMATECH
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Abstract: This report documents the results of a project to gather process-specific perfluorocompound (PFC) emissions data from commonly used tools to help SEMATECH's member companies determine their PFC emissions baseline. A variety of chamber cleaning and etch processes was analyzed. Electron impact ionization (EI) quadrapole mass spectrometry (QMS) was used to test for perfluoromethane (CF_4), perfluoroethane (C_2F_6), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), trifluoromethane (CHF_3), and perfluoropropane (C_3F_8). PFC byproducts were also identified and quantified. This revision is a nonconfidential version of the original report.

Keywords: Emissions, Perfluorocompounds, Gases, Etching, Chamber Cleaning, Byproduct Characterization

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1 EXECUTIVE SUMMARY

The objective of this project was to gather priority tool and process-specific perfluorocompound (PFC) emissions data to help SEMATECH’s member companies determine their PFC emissions baseline. In addition to determining the input PFC utilization efficiency, PFC byproducts were also identified and quantified.

The following processes were monitored:

Chamber Cleans

Novellus Concept One dielectric
Applied Materials 5000 TEOS
Applied Materials 5000 tungsten
Applied Materials 5000 SACVD
Applied Materials 5000 BPSG passivation/nitride

Etch

Matrix 303 isotropic via etch
Tegal 901 nitride
Applied Materials 5000 oxide etch
Applied Materials 8330 metal etch
Lam 4500 planarization etch
Applied Materials 8110 anisotropic via etch
Tegal 903 passivation etch

Electron impact ionization (EI) quadrapole mass spectrometry (QMS) was used to test for perfluoromethane (CF_4), perfluoroethane (C_2F_6), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), trifluoromethane (CHF_3), and perfluoropropane (C_3F_8).

1.1 Results – Chamber Cleans

PFC emissions were characterized from the Novellus Concept One and the Applied Materials 5000 during chamber cleaning after chemical vapor deposition (CVD) of a variety of film types. Chamber cleaning steps using C_2F_6 resulted in the formation of significant amounts of CF_4 (from 4.9 ± 1.6% to 17 ± 2.0% by mass of $C_2F_{6\ in}$).

In the Novellus Concept One, film type did not appear to change PFC utilization efficiency or the quantity of PFC byproducts formed. C_2F_6 utilization was approximately 31% by mass for the first step and 33% for the second step for all film types. CF_4 formation was approximately 11% by mass of $C_2F_{6\ in}$ for Step 1 and 17% of $C_2F_{6\ in}$ for Step 2 across all film types.

Data on an Applied Materials 5000 system suggests that film thickness may affect C_2F_6 utilization and the quantity of PFC byproducts, where an increase in film thickness increases C_2F_6 utilization and decreases CF_4 production. However, this difference might be due to using two different chambers and to measurement error. Further testing to determine the effect of film thickness on emission rates is suggested.

Data from the Applied Materials 5000 NF_3 doped C_2F_6 chamber cleaning processes revealed a decrease in C_2F_6 emissions from 80.1 ± 1.7% by mass of $C_2F_{6\ in}$ in the first step (which uses C_2F_6 only) to 74.9 ± 1.8% by mass of $C_2F_{6\ in}$ for the second step (which is doped with NF_3). However, this difference is small and may be due to measurement error. Also, because the steps correspond to different points in the chamber cleaning, parameters other than the addition of NF_3 might be influencing the results.

The use of NF_3 in the Applied Materials 5000 tungsten chamber cleaning system varied significantly from one tool to another because of differences in the recipes and chamber conditions. This suggests that for a given tool type and process, the gas emission rate may depend on the process recipe.

CF_4 exhibited an extremely low utilization efficiency in chamber cleaning with 94.5 ± 0.4% by mass passing through the process unreacted.

1.2 Results – Etch Processes

Etch processes used a variety of PFCs, either alone or in combination with other PFCs. The data suggest that PFC emission rates from etch processes depend on process recipes and chamber conditions. SF_6 emissions varied widely and depended on power levels and flow rates. NF_3 utilization in the Matrix 303 was extremely high at 84.0 ± 0.4%, which was significantly different from the NF_3 utilization rates reported for chamber cleaning applications. Etch processes using CF_4 and/or CHF_3 resulted in the formation of significant quantities of C_2F_6 and CF_4.

2 INTRODUCTION

In semiconductor manufacturing, perfluorocompounds (PFCs) such as perfluoromethane (CF_4), perfluoroethane (C_2F_6), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), trifluoromethane (CHF_3, and perfluoropropane (C_3F_8) are used in plasma etch and chamber cleaning applications. These gases are extremely long-lived compounds, having the ability to persist in the atmosphere for thousands to tens of thousands of years [1]. In addition, PFCs are strong infrared absorbers and have been identified as potentially significant contributors to global warming [1]. Because of this potential impact, the U.S. Environmental Protection Agency (EPA) has requested that members of the semiconductor industry voluntarily join their PFC Emission Reduction Partnership for the Semiconductor Industry. This program allows participants to identify and evaluate innovative ideas to achieve PFC emissions reductions and to choose individualized, cost-effective solutions for implementation in a specific fab. Companies that join the partnership must estimate PFC emissions annually beginning with 1995. Future emission reductions will be determined by comparison with the normalized 1995 baseline.

Currently, very limited data on tool emissions exists. Previous studies have compared input and output concentration of the PFC feedstock [2]. The difference between these concentrations has generally been referred to as the utilization efficiency. No attempts have been made to determine and quantify the products of utilization. Modeling the PFC plasma chemistry has indicated that these products probably include other PFC compounds. Therefore, the utilization efficiency alone is insufficient to characterize the potential global warming impact of a process.

The objective of this project was to gather priority tool and process specific PFC emissions data, which could be used by SEMATECH member companies in determining their PFC emissions baseline. In addition to determining the input PFC utilization efficiency, PFC byproducts were also identified and quantified.

3 POLICIES REGARDING PFC EMISSIONS

3.1 Framework Convention on Climate Change

In 1992 world leaders and citizens from more than 200 countries came together in Rio de Janeiro, Brazil, at the Earth Summit to discuss the global ecological crisis. There, the U.S. and 160 other nations signed an international agreement, the Framework Convention on Climate Change (FCCC), committing to develop national plans to manage and limit greenhouse gas emissions. The objective of this agreement was to

> “... achieve ... stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Such a level should be achieved within a timeframe sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened, and to enable economic development to proceed in a sustainable manner.”

3.2 Climate Change Action Plan

To fulfill the commitment of the FCCC, President Clinton released the Climate Change Action Plan in 1993, which defines the U.S. program for managing and limiting greenhouse gas emissions. This comprehensive plan targets all greenhouse gases, including PFCs, and all sectors of the economy. It calls for partnerships between the government and the private sector to promote creative, flexible, cost-effective approaches to emissions reductions, as opposed to “relying exclusively on command-and-control mandates that tend to lock technologies into place and stifle innovation.”

In alignment with this plan, the EPA has requested that the semiconductor industry participate in a voluntary PFC emissions reduction program, which would allow participants the freedom to design an individualized emissions reduction strategy. The gases addressed by this program are perfluoromethane (CF_4), perfluoroethane (C_2F_6), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), trifluoromethane (CHF_3) and perfluoropropane (C_3F_8). The industry, represented by a subcommittee of the Semiconductor Industry Association (SIA), worked with the EPA to develop a basic format agreement for this program entitled the PFC Emission Reduction Partnership for the Semiconductor Industry. The partnership and program details are described in a Memorandum of Understanding (MOU), which is being sent to all semiconductor manufacturing companies with operations in the U.S.

It is a distinct possibility that if the semiconductor industry does not show serious effort in trying to achieve PFC emissions reductions, the availability and use of these gases will be restricted in the U.S.

3.3 EPA’s MOU – Agreements, Principles, and Responsibilities

3.3.1 Common Agreements and Principles

This section of the MOU states that both parties agree that the industry relies on PFCs to manufacture semiconductors and that to date there are no proven substitutes that satisfy the unique performance characteristics of PFCs. Furthermore, any restrictions on the availability of PFCs could significantly affect the industry’s ability to compete in a global market. Both parties commit to working toward reducing PFC emissions associated with manufacturing semiconductor devices in the U.S., and, if possible, replacing them with compounds that do not trigger global warming concerns or other potentially adverse effects. The section acknowledges that recycling, abatement, and other control technologies are still in the early development stage and have yet to be proven for PFC applications. It also states that actual emissions data are not available, and there is currently no agreed-upon physical monitoring method.

3.3.2 EPA Responsibilities

The EPA will seek commitments from all companies with semiconductor operations in the U.S., including foreign-owned companies. It will also encourage governments of other countries with significant semiconductor manufacturing industries to adopt a similar voluntary program. The EPA will conduct preliminary assessments to determine the potential for substitute chemicals to be greenhouse gases and will serve as a technical clearinghouse for non-confidential information on successful strategies for reducing PFC emissions. Finally, it will publicly recognize participants in the program and will inform them in advance of any steps that might be taken by the Office of Atmospheric Programs regarding the use and availability of PFCs, as these steps relate to global warming concerns.

3.3.3 Company Responsibilities

Companies participating in the Program will prepare two estimates of PFC emissions annually: an overall estimate of their aggregate PFC emissions and a PFC emission rate per unit of production, which has been normalized against the 1995 baseline, to prevent the distorting effect caused by overall increases in production and/or chip complexity. These values will be delivered to a designated law firm, which will then release the data to the EPA on a company-blind basis. Reports will be due to the law firm on July 1 each year. Although it has not been documented in the MOU, the first reporting period for 1995 emissions was extended until November 15, 1996, to allow participants to more accurately determine their baseline PFC emissions.

In addition to reporting emissions estimates, participants will endeavor to reduce the rate of emissions through process optimization, reclaim/recycle, abatement, and replacement chemistries (if possible), but no specific reduction target is mentioned. However, companies will reconvene with the EPA in two years to discuss whether specific reduction targets can be committed to based on the status of research and development efforts. Finally, participants will agree to share any non-confidential information about successful PFC emissions reductions processes and technologies and will extend PFC reduction strategies to overseas operations at their discretion.

3.3.4 Other Issues

This section states that both parties agree to formally notify each other if a problem arises and that any information submitted as part of the program will be treated according to 40 CFR, Part 2, including provisions protecting confidential business information.

The MOU expires on December 31, 2000.

4 TESTING STRATEGY

Key tools and processes in plasma etch and chamber cleaning were targeted for testing. SEMATECH collected information from member companies on their priority tools and corresponding processes needing PFC emissions characterization. A subset of the original list was chosen for testing based on tool and funding availability. Testing was done during wafer processing, thereby precluding a design of experiment with varying process parameters. A condition for conducting this project was that proprietary information such as process recipes and process conditions would not be included in this report. Only tool PFC emissions factors would be reported. The only gases that would be identified and quantified were the PFCs subject to the MOU; thus, a fluorine and carbon mass balance could not be completed since the analyses did not identify or quantify all carbon- and fluorine-containing species. The emission rate of input PFCs would be reported as a percentage of their usage rate, and emission rates of byproducts would be reported in terms of the percentage of the total mass or volume of the input PFCs.

5 SAMPLING AND ANALYTICAL PLAN

5.1 Analysis Method and Instrumentation

All sampling was performed by Air Products and Chemicals Inc. (APCI) using electron impact ionization (EI) quadrapole mass spectrometry (QMS). The QMS was a UTI Qualitrace III equipped with a special high pressure inlet system and closed ion source. It was operated in selective ion monitoring (SIM) mode for quantitative determinations of PFCs. The only gases quantified and reported were the PFCs subject to the terms of the MOU. All samples were taken downstream of the process tool vacuum systems. The sampling frequency was typically one sample per three seconds.

5.2 Sampling Methodology

The sampling scheme for the QMS analysis is shown in Figure 1. Samples were drawn through 0.125” stainless steel tubing from 0.25” stainless steel Swaglock or VCR fittings welded directly to the process exhaust lines. Samples were drawn through the QMS source using a mechanical sampling pump. The pumping speed was controlled by throttle valve (T) located on the exit of the source to yield a sampling pressure of about 720 Torr. Under these sampling conditions, the flow rate through the source was about 0.5–1.0 slpm. The pressure was monitored with a capacitance manometer (P) located immediately downstream of the QMS source. Exhausts from the QMS and the sampling pump were teed together and vented from the sub-fab through the house scrubbed exhaust system.

5.3 Calibration

The response of the QMS to selected compounds was directly calibrated using a dynamic dilution calibration system. Test atmospheres containing 400–10,000 parts per million by volume (ppmv) of C_2F_6, NF_3, CF_4, SF_6, and CHF_3 in nitrogen were prepared by diluting a 1% mixture in nitrogen. Linear regression analyses of these data yielded QMS response factors for specific analytes.

The QMS was calibrated before and after each set of wafers (i.e., 10–20 wafers on a single tool or 1–2 lots on a batch tool) monitored. Frequent calibrations were necessary to ensure the accuracy of reported concentrations.

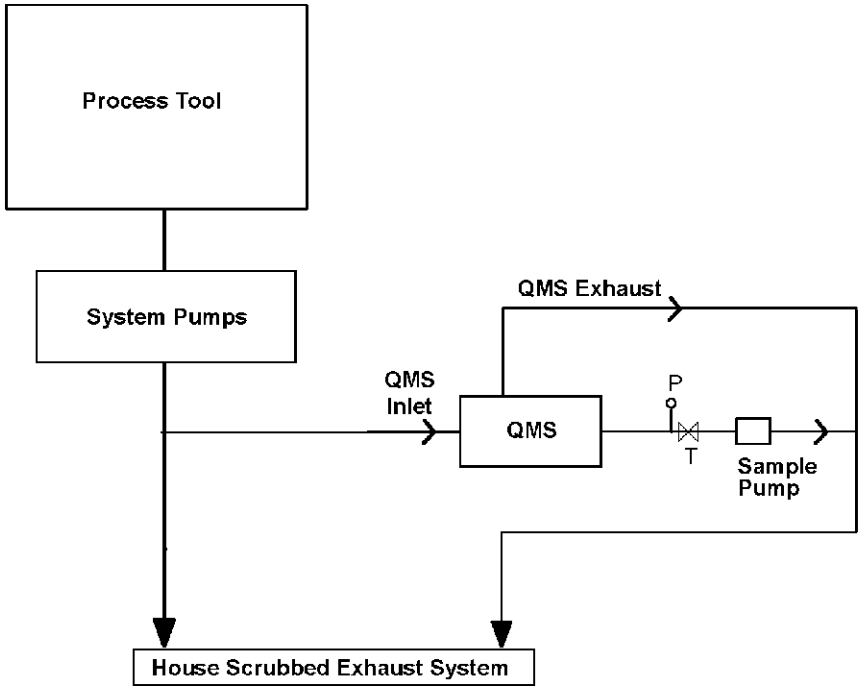

Figure 1 Schematic of Sampling Equipment Installation

5.4 Baseline Emissions

Emission factors were identified after determining PFC emissions under conditions in which no PFCs were consumed or created. These conditions were achieved by flowing process gases at the process recipe flow rates with radio frequency (RF) power turned off. All reported utilization efficiencies are relative to the baseline emissions determined for a particular process. Baseline emissions were particularly important in analyses of process tools using mechanical pumps containing perfluorinated oils (wet pumps). These older pumping systems typically have low pump purge volumes resulting in the stagnation of gases exiting the pump. Since the PFC concentration in the exhaust never reaches steady state, efficiency could not be based directly on a ratio of effluent concentrations. In these cases, it was necessary to integrate PFC emissions during processing and calculate utilization efficiency relative to the integrated baseline emissions.

5.5 Calculations

The utilization efficiency of an input gas was determined from the difference between the tool emission rate of that gas with and without the plasma on in the process tool. Emission rates of all byproduct PFCs were calculated in terms of their percent by volume and by mass of the total influent PFC stream. The following formulas were used in the calculations:

$$Utilization\ Efficiency\ (UE) = \left[\frac{\left(C_{plasma\ off} - C_{plasma\ on}\right)}{C_{plasma\ off}}\right] \times 100$$

where C = Measured Concentration of Input PFC

$$\%\ Input\ PFC\ Emitted = 100 - UE$$

$$\%\ PFC_i\ Created\ by\ Volume = \left[\frac{Volume\ of\ PFC_i}{Total\ Input\ PFC\ Volume}\right] \times 100$$

$$\%\ PFC_i\ Created\ by\ Mass = \left[\frac{Mass\ of\ PFC_i}{Total\ Input\ PFC\ Mass}\right] \times 100$$

6 RESULTS

6.1 Chamber Cleaning Processes

PFC emissions data were collected from cleaning a variety of film types in the Novellus Concept One and Applied Materials 5000 chemical vapor deposition (CVD) systems, both of which are common in the industry’s installed tool base. The films in the Novellus tool included a phosphorous doped tetraethylorthosilicate (PTEOS) based oxide, a plasma enhanced oxide/boron phosphorus silicate glass (PEO/BPSG), and a phosphorus silicate glass (PSG). Films and/or processes in the Applied Materials 5000 tools included tetraethylorthosilicate oxide (TEOS/oxide), sub-atmospheric chemical vapor deposition (SACVD), tungsten, and phosphorus silicate glass (PSG)/nitride passivation. When possible, cleans of a variety of film thicknesses were also characterized in these tools. C_2F_6 is the gas used in greatest quantity for chamber cleans. Table 1 lists the results of chamber cleans using C_2F_6. Table 2 lists results of a clean using C_2F_6 for the first step and C_2F_6 doped with NF_3 for the second. Table 3 lists results obtained on two different Applied Materials 5000 tungsten deposition systems using NF_3 with different process conditions and a CF_4 chamber clean on an Applied Materials 5000 PSG/nitride passivation deposition system.

Table 1 PFC Emissions from C_2F_6 Chamber Cleaning Processes

Tool	Process		Input PFC(s)	C_2F_6 Out (Volume % of C_2F_6 in)	CF_4 Out (Volume % of C_2F_6 in)	C_2F_6 Out (Mass % of C_2F_6 in)	CF_4 Out (Mass % of C_2F_6 in)
Novellus Concept One	PTEOS:	Step 1	C_2F_6	69 ± 1.6	17 ± 5.2	69 ± 1.6	11 ± 3.3
		Step 2	C_2F_6	66 ± 1.5	27 ± 2.4	66 ± 1.5	17 ± 1.5
Novellus Concept One	PEO/BPSG:	Step 1	C_2F_6	69 ± 1.6	15 ± 8.3	69 ± 1.6	10 ± 5.3
		Step 2	C_2F_6	67 ± 1.6	27 ± 3.1	67 ± 1.6	17 ± 2.0
Novellus Concept One	PSG:	Step 1	C_2F_6	70 ± 2.0	17 ± 7.6	70 ± 2.0	11 ± 4.8
		Step 2	C_2F_6	67 ± 1.6	27 ± 3.1	67 ± 1.6	17 ± 2.0
Applied Materials 5000	x K* TEOS/Oxide		C_2F_6	75.8 ± 0.7	13.4 ± 0.8	75.8 ± 0.7	8.5 ± 0.5
Applied Materials 5000	4x K* TEOS/Oxide		C_2F_6	65.9 ± 1.6	7.6 ± 2.4	65.9 ± 1.6	4.9 ± 1.6

* Denotes the film thickness. One is 4x the thickness of the other.

Table 2 PFC Emissions from NF_3 Doped C_2F_6 Chamber Cleaning Process

Tool	Process	Input PFC(s)	C_2F_6 Out (Volume % of C_2F_6 in)	CF_4 Out (Volume % of C_2F_6 + NF_3 in)	NF_3 Out (Volume % of NF_3 in)	C_2F_6 Out (Mass % of C_2F_6 in)	CF_4 Out (Mass % of C_2F_6 + NF_3 in)	NF_3 Out (Mass % of NF_3 in)
Applied Materials 5000	SACVD							
	Step 1	C_2F_6	80.1 ± 1.7	12.4 ± 1.6		80.1 ± 1.7	7.9 ± 1.0	
	Step 2	C_2F_6, NF_3	74.9 ± 1.8	17.2 ± 2.4	35.9 ± 0.9	74.9 ± 1.8	7.6 ± 1.0	35.9 ± 0.9

Table 3 PFC Emissions from NF_3 and CF_4 Chamber Cleaning Processes

Tool	Process	Input PFC(s)	NF_3 Out (Volume % of NF_3 in)	CF_4 Out (Volume % of CF_4 in)	NF_3 Out (Mass % of NF_3 in)	CF_4 Out (Mass % of CF_4 in)
Applied Materials 5000	Tungsten	NF_3	67.6 ± 1.3		67.6 ± 1.3	
Applied Materials 5000	Tungsten	NF_3	40.3 ± 2.1		40.3 ± 2.1	
Applied Materials 5000	PSG Passivation Nitride	CF_4		94.5 ± 0.4		94.5 ± 0.4

6.2 Etch Processes

Etch tools and processes vary much more widely than CVD tools and plasma chamber cleaning processes. A variety of etch tools running different processes were examined. Table 4 lists results of characterizations of etches using a single PFC that does not contain carbon. Table 5 lists results of etches using only carbon- and fluorine-based PFCs as input chemistries. Table 6 lists results from a Tegal 903 passivation etch using a variety of PFCs in different etch steps.

Table 4 PFC Emissions from NF_3 and SF_6 Etch Processes

Tool	Process	Input PFC(s)	NF_3 Out (Volume % of NF_3 in)	SF_6 Out (Volume % of CF_4 in)	NF_3 Out (Mass % of NF_3 in)	SF_6 Out (Mass % of CF_4 in)
Matrix 303	Isotropic Via Etch	NF_3	16.0 ± 0.4		16.0 ± 0.4	
Tegal 901*	Nitride Etch	SF_6		79.2 ± 17.3		79.2 ± 17.3

* A variety of process conditions was run. Standard deviation reflects the averaging of results, not precision of measurements.

Table 5 PFC Emissions from Plasma Etch Processes Using CHF_3 and/or CF_4

Tool	Process	Input PFC(s)	**CHF_3 Out** (Volume % of CHF_3 in)	**CF_4 Out** (Volume % of CF_4 in)	**C_2F_6 Out** (Volume % of CHF_3 + CF_4 in)	**CHF_3 Out** (Mass % of CHF_3 in)	**CF_4 Out** (Mass % of CF_4 in)	**C_2F_6 Out** (Mass % of CHF_3 + CF_4 in)
Applied Materials 5000	Oxide Etch	CHF_3, CF_4	59.6 ± 10.1	306.4 ± 79.0	2.0 ± 1.34	59.6 ± 10.1	306.4 ± 79.0	3.8 ± 2.24
Applied Materials 8330	Metal Etch	CHF_3, CF_4	59.2 ± 3.6	79.1 ± 5.7	7.7 ± 0.4	59.2 ± 3.6	79.1 ± 5.7	4.8 ± 1.1
Lam 4500	Planarization Etch	CHF_3, CF_4	76.1 ± 0.7	99.5 ± 1.9	2.7 ± 0.1	76.1 ± 0.7	98.9 ± 1.2	1.8 ± 0.2
Tool	**Process**	**Input PFC(s)**	**CHF_3 Out** (Volume % of CHF_3 in)	**CF_4 Out** (Volume % of CHF_3 in)	**C_2F_6 Out** (Volume % of CHF_3 in)	**CHF_3 Out** (Mass % of CHF_3 in)	**CF_4 Out** (Mass % of CHF_3 in)	**C_2F_6 Out** (Mass % of CHF_3 in)
Applied Materials 8110	Anisotropic Via Etch*	CHF_3	40	8.0	3.0	40	10	6.0

* This was a single point evaluation; therefore, no standard deviation is shown.

Table 6 PFC Emissions from Tegal 903 Passivation Etch Process*

Input PFC(s)	**C_2F_6 Out** (Volume % of inputs)	**CF_4 Out** (Volume % of inputs)	**CHF_3 Out** (Volume % of CHF_3 in)	**SF_6 Out** (Volume % of SF_6)	**C_2F_6 Out** (Mass % of inputs)	**CF_4 Out** (Mass % of inputs)	**CHF_3 Out** (Mass % of CHF_3 in)	**SF_6 Out** (Mass % of SF_6)
C_2F_6	50 ± 20.3 (a)	56.7 ± 12.3 (a)			50 ± 20.3 (a)	36.1 ± 7.9 (a)		
SF_6				46.0 ± 48.1				
SF_6, CHF_3	6.8 ± 1.3 (b)	19.3 ± 5.8 (b)	50.3 ± 4.6	11.3 ± 1.5	5.79 ± 2.8 (b)	21.2 ± 6.7 (b)	50.3 ± 4.6	46.0 ± 48.1
C_2F_6, CHF_3	49.7 ± 6.7 (a)	35 ± 1.0 (c)	80.7 ± 15.3		49.7 ± 6.7 (a)	27.8 ± 2.5 (c)	80.7 ± 15.3	11.3 ± 1.5

(a) input chemistry = C_2F_6

(b) input chemistry = CHF_3 + SF_6

(c) input chemistry = C_2F_6 + CHF_3

*A variety of processes conditions was run. Standard deviation reflects the averaging of results, not precision of measurements.

7 SUMMARY AND CONCLUSIONS

The data presented in this report will help SEMATECH member companies estimate their PFC emissions baseline with a greater degree of accuracy than using PFC utilization data alone; however, additional emissions characterizations should be undertaken by the tool suppliers to help refine the numbers presented.

7.1 Chamber Cleaning Processes

PFC emissions were characterized from the Novellus Concept One and the AMAT 5000 cleaning a variety of film types. As seen in Table 1 and Table 2, chamber cleaning steps using C_2F_6 resulted in the formation of significant amounts of CF_4 (from 4.9 ± 1.6 % to 17 ± 2.0% by mass of $C_2F_{6\ in}$).

In the Novellus Concept One, film type did not appear to change PFC utilization efficiency or the quantity of PFC products (see Table 1). C_2F_6 utilization was approximately 31% by mass for Step 1 and approximately 33% for Step 2 cleans for all film types. CF_4 formation was approximately 11% by mass of $C_2F_{6\ in}$ for Step 1 and 17% of $C_2F_{6\ in}$ for Step 2 across all film types.

Data on an Applied Materials 5000 system suggests that film thickness may affect C_2F_6 utilization and the quantity of PFC byproducts, where an increase in film thickness increases C_2F_6 utilization and decreases CF_4 production (see Table 1). However, this difference might be due to using two different chambers and to measurement error. Further testing to determine the effect of film thickness on emission rates is suggested.

Data from the Applied Materials 5000 NF_3 doped C_2F_6 chamber cleaning processes revealed a decrease in C_2F_6 emissions from 80.1 ± 1.7 % by mass of $C_2F_{6\ in}$ in the first step (which uses C_2F_6 only) to 74.9 ± 1.8 % by mass of $C_2F_{6\ in}$ for the second step (which is doped with NF_3). However, this difference is small and may be due to measurement error. Also, because the steps correspond to different points in the chamber cleaning, parameters other than the addition of NF_3 might be influencing the results.

In Table 3, the use of NF_3 in the AMAT 5000 tungsten chamber cleaning system varied significantly from one tool to another because of differences in the recipes and chamber conditions. This suggests that it might not be wise to assume that for a given tool type and process, the gas emission rate is independent of the process recipe.

CF_4 exhibited an extremely low utilization efficiency in chamber cleaning with 94.5 ± 0.4 % by mass passing through the process unreacted.

7.2 Etch Processes

Etch processes used a variety of PFCs, either alone, or in combination with other PFCs. The data suggest that PFC emission rates from etch processes depend on process recipes and chamber conditions. SF_6 emissions varied widely and depended on power levels and flow rates. NF_3 use in the Matrix 303 was extremely high at 84.0 ± 0.4 %, which was significantly different from NF_3 use rates reported for chamber cleaning applications. As seen in Table 5 and Table 6, etch processes using CF_4 and/or CHF_3 resulted in the formation of significant quantities of C_2F_6 and CF_4.

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