

Improving the Environmental Performance of *In Situ* PECVD Chamber Cleaning Processes by studies of CVD Reactor Clean Performance and Field Evaluation of Optimised Processes

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Abstract

Using a common production platform and process (Applied Materials P-5000 D_xL, 1.0 μm TEOS), laboratory studies demonstrated that the standard C₂F₆ recipe can be successfully optimised, resulting in significant reductions in emissions (51%) and gas usage (40%). Optimised clean recipes for alternative fluorocarbon gases (C₃F₈, C₄F₈ and C₄F₈O) yield similar reductions but exhibit no significant performance advantages over C₂F₆, when optimised processes are compared. Significant improvements are observed over the standard C₂F₆ recipe for a dilute NF₃ process (94% and 77% reduction in emissions and gas usage respectively, 11% reduction in clean time). These laboratory findings are supported by field evaluation studies with semiconductor manufacturers. Optimisation of existing chemistry produces significant improvements in environmental performance and cost savings with simpler process qualification and no need for hardware changes. The improvements afforded by the optimised C₂F₆ process can also be extended to other cleaning processes that use CF₄ by substituting C₂F₆ for CF₄.

1 Introduction

Carbon based perfluorocompounds such as C₂F₆ are widely used in the semiconductor industry.¹⁻³ The potential impact of these molecules on global warming has become an increasing concern in recent years.¹⁻⁶ Major semiconductor manufacturers and the U. S. Environmental Protection Agency (EPA) have issued a memorandum of understanding (MOU) that calls for a voluntary reduction or elimination of PFC emissions.⁷ In addition, the World Semiconductor Council has declared an industry-wide goal of 10% reduction of PFC emissions (MMTCE-Tonnes of Carbon Equivalent) by 2010 based on 1995 emissions.^{7,8}

Although estimates vary, it is generally accepted that over 70% of the PFCs emitted from the semiconductor manufacturing processes are derived from in situ cleaning of residues from the chamber walls inside plasma-enhanced chemical vapour deposition (PECVD) reactors. PFC emissions arise from both the undestroyed PFC feed gas and the plasma-generated CF₄. Several approaches to reduce PFC emissions during PECVD chamber cleaning are being pursued. These approaches include:

- 1) Optimising C₂F₆-based in situ cleaning;^{9-12,20,21,23}

- 2) Replacing C₂F₆ with an alternative PFC for in situ cleaning;¹³⁻¹⁶
- 3) Utilising dilute NF₃ for in situ cleaning;¹⁷
- 4) Adopting NF₃-based remote downstream cleaning technology.¹⁸⁻¹⁹

Although emissions for new PECVD systems are virtually eliminated by adoption of 4), legacy systems can benefit from investigation of 1) through to 3). Chamber cleaning performance depends on reactor, film composition, and various process parameters. Process optimisation is a balancing act. Trade-offs between lower MMTCE and other important factors such as shorter clean time must be considered.

This paper reports on PECVD in situ chamber cleaning studies performed on a common production platform (Applied Materials P-5000 D_xL chamber) following a 1.0 μm TEOS oxide deposition using the following fluorine-containing gases: C₂F₆, C₃F₈, C₄F₈, C₄F₈O, and NF₃.

For each cleaning gas, a design of experiments (DOE) was performed to determine the optimised cleaning process with regards to feed gas flow rates, O₂/PFC ratio, process pressure, and RF power. The cleaning time, gas usage, PFC destruction efficiency, and global warming impact (MMTCE) under optimised

cleaning conditions were then evaluated for each gas relative to the standard C_2F_6 process.

Examples of field optimisation studies at major semiconductor manufacturing facilities in Europe²⁰⁻²⁴ are also presented, demonstrating how significant environmental benefits can be gained by deploying optimised processes in production fabs.

2 Optimisation of the TEOS PECVD Chamber Clean Process

Clean processes following TEOS PECVD deposition were optimised using a central composite design of experiments (DOE) methodology. DOE parameters were: Cleaning gas flow-rate, oxygen ratio (helium in the case of NF_3) pressure and power. The relationship between clean time and PFC emissions for DOE parameters were obtained from each set of experiments.

The concentrations of PFC by-products during CVD chamber cleans were measured using quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy. Process by-products were sampled downstream of the CVD chamber pump exhaust at ambient pressure and were diluted by the N_2 pump purge (Figure 1).

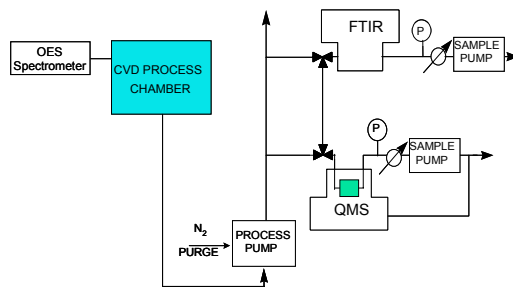


Figure 1: Process and analytical layout.

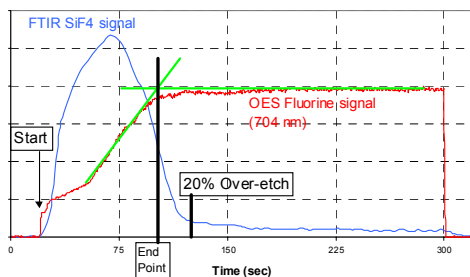


Figure 2: Endpoint monitoring.

Clean times were determined from the optical emissions spectrometer (OES) end-point monitor at the CVD chamber and the SiF_4 profile from the chamber clean (figure 2). During cleaning, there is little light

emission as F-atoms are consumed by etching, indicated by the increasing SiF_4 concentration. As the CVD residue clears, however, the F-atom density increases resulting in an intense emission line. The clean times were taken as the time for the OES to reach end point plus a 20% over-etch.

Emissions from the chamber clean were obtained by integrating under the measured concentration profiles, and quantified using the following relationship:

$$MMTCE = \sum_{PFC} \frac{Q(kg) \cdot (\frac{12}{44}) \cdot GWP_{100}}{10^9}$$

All by-products having a non-zero global warming potential (GWP_{100}) are included in the MMTCE calculation.

In all comparisons between chamber cleans and cleaning chemistries, it is important to ensure that the chamber has been fully cleaned. Hence, the amount of CVD residue (measured as SiF_4) removed should be equivalent to that removed by the existing 'standard' clean process.

3 C_2F_6 Optimisation

Before making any comparison of cleaning performance between candidate chamber cleaning gases, it is very important to first of all ensure that the existing clean chemistry is optimised, otherwise comparisons will be on an unequal basis. Table 1 shows the process space evaluated for the C_2F_6 optimisation to compare with the existing standard recipe as supplied by the tool manufacturer.

DOE Parameters			
C_2F_6 flow (sccm)	O ₂ /PFC	Pressure (torr)	Power (W)
200-600	0.5-1.5	4-6	650-950
Standard C_2F_6 recipe			
600	1	4	950

Table 1: C_2F_6 Process Space Evaluated.

From the experiments, response surfaces were constructed to evaluate the sensitivity of the clean performance to the DOE parameters. For example (figure 3), lower emissions were favoured by lower C_2F_6 flow-rates and higher power settings. Similar plots show that increasing C_2F_6 flow-rate and power can reduce clean time. Also, it was found, O₂/PFC ratio influenced clean time and emissions both positively and negatively, while increasing pressure reduced clean times and marginally increased emissions.

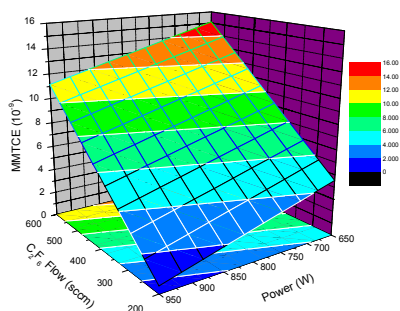


Figure 3: Response Surface from C₂F₆ Optimisation

Figure 4 illustrates the optimal conditions in comparison to the standard process. A 36% reduction in emissions (MMTCE) and 33% reduction in gas usage resulted in a clean time equal to the standard C₂F₆ process. A further reduction in emissions (51%) was achievable by reducing gas flow further (40%) at the expense of a 20% longer clean time. Increasing power to 1150W brought the clean time back to be equivalent to the standard clean with 59% and 48% reductions in MMTCE and gas usage.

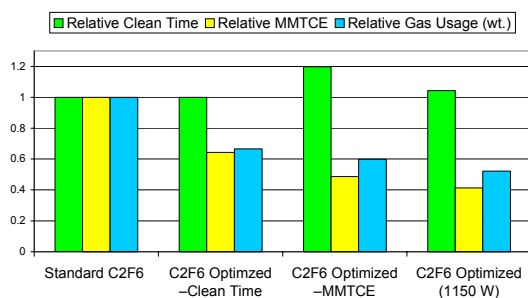


Figure 4: Results of C₂F₆ optimisation.

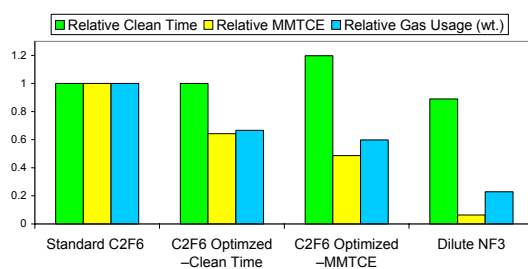


Figure 5: Results of NF₃ Optimisation.

4 NF₃ Optimisation

Dilute NF₃ (balance helium) was used to compare with optimised C₂F₆. The parameter space investi-

gated was as follows: NF₃ (200-400 sccm), NF₃/He (10-25%), Pressure (2-4 torr) and power (950 W).

Compared to the standard C₂F₆ process (figure 5), NF₃ reduced the clean time by 11 %, reduced emissions by 94% and, overall, reduced gas usage by 77%.

5 Alternative Fluorocarbon Optimisation Study

The cleaning performance of some common alternative fluorocarbons (C₃F₈, C₄F₈ and C₄F₈O) was evaluated over the parameter range in Table 2. The performance of C₃F₈ and C₄F₈ was also measured at conditions reported in the literature to be favourable¹⁶.

	Flow (sccm)	O ₂ /PFC	Pressure (torr)	Power (W)
C ₃ F ₈	100-400	1-5	4-6	650-950
C ₄ F ₈	100-400	3-5	4-6	650-950
C ₄ F ₈ O	100-400	2-5	4-6	650-950
C ₃ F ₈ ⁽¹⁶⁾	211	2.13	5	750
C ₄ F ₈ ⁽¹⁶⁾	169	4.56	5	750

Table 2: DOE Parameters for alternative fluorocarbon study.

The results of the evaluation show that gas usage and, with the exception of C₄F₈, clean times are comparable to an optimised C₂F₆ clean process (figure 6). Comparison of the effluent emissions from the different cleans (figure 7) shows, again, comparable performance to the optimised C₂F₆ process. The dilute NF₃ clean remains the fastest with the lowest environmental impact and highest efficiency in terms of weight of gas used per clean.

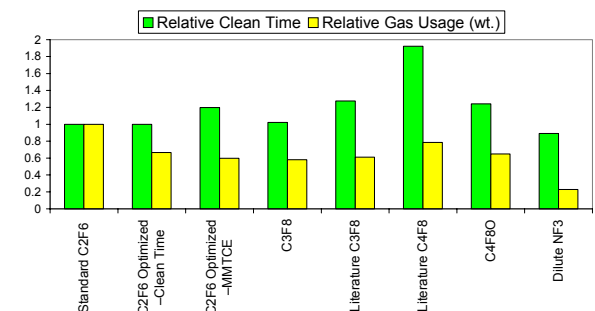


Figure 6: Summary of clean times and gas usage for all chamber clean gases.

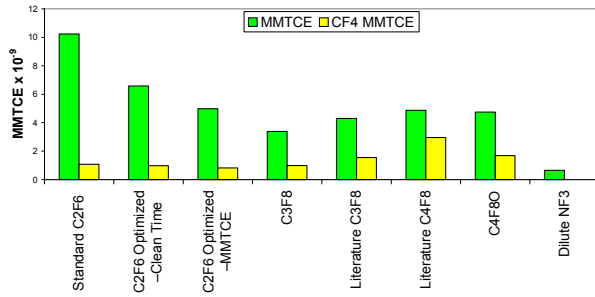


Figure 7: Summary of effluent emissions from all chamber clean gases.

6 Field Optimisation Studies

Numerous studies of field optimisation work have been reported,²⁵ of which key examples, involving European based semiconductor manufacturers, are discussed briefly here²⁰⁻²⁴.

6.1 Cleaning Silane Based PECVD Films: Optimisation of C₂F₆ and C₄F₈ Processes.

C₂F₆ and C₄F₈ cleans were evaluated as a alternative to a CF₄ based clean which was used following a silane based SiNx deposition in an Applied Materials DxL (lamp heated) chamber^{22, 24}. CF₄ as a cleaning gas is notoriously inefficient with approximately 95% remaining unutilised from the clean, consequently emitting significant quantities of CF₄, which has high global warming potential (GWP₁₀₀ 6500) and long atmospheric lifetime (>50000 years)²⁶.

A full design of experiments (Table 3) was conducted to evaluate the performance of C₂F₆ and C₄F₈.

	C ₂ F ₆ DOE	C ₄ F ₈ DOE
Flow rate (sccm)	300 – 700	50 – 200
N ₂ O:PFC ratio	1.5 – 3.5	8 – 10
Pressure (torr)	2.0 – 5.0	3.5 – 5.5
Power (W)	800	500 – 800

Table 3: Parameter space for silane based film DOE (lamp heated chamber).

Both cleaning gases gave equivalent performance in terms of clean time and emissions (Table 4), but, problems with a weak end point signal from the tool OES and mass flow controller instability indicated that C₄F₈ was not a feasible drop in replacement for the CF₄ based clean. Also, it was found from the DOE results that C₄F₈ cleans were not removing the entire CVD residue from the chamber. To try to overcome this, power was increased to 1000W and flow rate to 300 sccm (Table 4).

	CF ₄ base	C ₄ F ₈	C ₂ F ₆
PFC (sccm)	1500	300	300
N ₂ O:PFC	0.5	10	2.5
P (torr)	5.0	2.9	3.5
Power (W)	800	1000	800
Clean time (s)	101	76	82
MMTCE	20 x 10 ⁻⁹	5.4 x 10 ⁻⁹	7.8 x 10 ⁻⁹
Gas used (g)	11.8	5.4	3.7

Table 4: Summary of DOE results for silane based PECVD films.

All C₂F₆ cleans effectively cleared the CVD residue from the chamber. Gas usage and PFC emissions were reduced by 68% and 61% respectively and the CVD chamber was cleaned some 18% faster. The C₂F₆ clean was selected as a true drop in replacement for CF₄ and it has been successfully qualified in production.

In a separately reported study²⁷, C₂F₆ was also used to achieve up to 63% reduction in emissions and 62% reduction in gas consumption on similar silane based films (SiNx, SiON, SiO) deposited in an inductively heated (as opposed to lamp heated) 200mm PECVD process. A 3000 wafer run marathon for each film type confirmed clean times, particles, deposition rate and refractive index to be essentially the same as the original CF₄ based clean.

6.2 Field C₂F₆ based optimisations.

The majority of the installed base of CVD tools uses C₂F₆ as the cleaning gas. Optimisation of the existing chemistry continues to be the best option for both environmental emissions reduction and cost reduction. These tools were initially installed before the drive to reduce emissions was fully recognised and they have therefore been operating for some time under non-optimal regimes. A short review of some recently published work by semiconductor manufacturers helps in appreciating how much can be achieved with these tools.

At a production facility containing a variety of Applied Materials and Novellus CVD based processes^{20, 23}, optimisation of a Novellus Concept-2 platform running USG, BPTEOS and SiNx films was undertaken as part of a site initiative to lower environmental impact, reduce inventories, reduce costs and also aid upgrading from 6 inch to 8 inch wafer processing. A process was identified which resulted in an emissions reduction of 42% with gas savings of 37% without impacting the clean time. Long-term drift of

film deposition properties was unaffected by the introduction of the new cleaning recipe.

Also using Novellus equipment (200mm Concept-2 Altus), a separate in-fab optimisation project involving the deposition of tungsten films²¹ identified several conditions with both good environmental and cost saving benefits (Table 5). This example demonstrates the flexibility often available from a C₂F₆ based clean process. Four options were identified following the completion of a full design of experiments.

A clean of comparable clean time to the existing clean process gave gas savings of 15% and reduced environmental emissions of 18%. A slightly longer clean operating at an even lower flow-rate yielded 27% gas savings and a 31% reduction in emissions. Increasing power and reducing C₂F₆ flow further resulted in 42% gas savings and 49% lower emissions with the benefit of a faster clean. Finally a clean 25% quicker than the base clean using high power and a higher C₂F₆ flow rate, still produced gas savings of 8% and an emissions reduction of 17%.

	C ₂ F ₆ (sccm)	Usage (%)	Time (%)	MMTCE (%)
Standard	1300	-	-	-
Same time	1100	-15%	-	-18%
Low MMTCE 1	850	-27%	+12%	-31%
Low MMTCE 2	800	-42%	-6%	-49%
Fast	1600	-8%	-25%	-17%

Table 5: Overview of clean options from tungsten deposition process.

7 Conclusions

Comparison of the relative clean performance of a number of chamber cleaning gases (C₂F₆, C₃F₈, C₄F₈, C₄F₈O and NF₃) on a single Applied Materials platform, revealed that significant reductions in gas savings and process emissions are possible by optimisation of the standard C₂F₆ clean process. Also, other than the dilute NF₃ clean, alternative PFC cleaning gases exhibit no significant performance advantages over C₂F₆ when compared to an optimised situation. The best performance is offered by a change to in-situ NF₃ cleaning.

When translated to the field, where the majority of the installed tool-base is using C₂F₆, the best solution is to optimise the existing clean chemistry. This simplifies the tool qualification process, eliminates any hardware changes and achieves substantial, immediate

cost savings and environmental benefits. Where CF₄ is used as the cleaning gas, the benefits and flexibility of a C₂F₆ clean can also be employed without the need for any hardware changes.

8 Literature

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