

OPTIMIZATION OF A C₂F₆ CLEAN FOR AN APPLIED MATERIALS' TEOS PECVD PROCESS: REDUCED PFC EMISSIONS AND FASTER CLEAN TIMES

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Semiconductor manufacturers are committed to reducing their emissions of perfluorocompounds (PFCs) because these gases have a high global warming potential. This paper describes how PFC emissions from an Applied Materials' TEOS PECVD process were reduced by optimizing the C₂F₆-based chamber clean. Our strategy was to measure response surfaces for the PFC emissions and clean time using a central composite design of experiments (DOE) methodology. Using these response surfaces, the process parameters (C₂F₆ flow rate, O₂:C₂F₆ ratio, and pressure) can be adjusted to minimize PFC emissions while maintaining an acceptable clean time. Volumetric PFC emissions were determined by both quadrupole mass spectrometry (QMS) and fourier transform infrared (FTIR) spectroscopy. The clean time was measured using optical end-point detection. For a 1.8 μm TEOS film, PFC emissions were reduced to 3.9×10⁻⁹ million metric tons carbon equivalent (MMTCE) while the clean time was shortened by 9-18 %. The optimized clean removes all of the TEOS residue from the PECVD chamber as indicated by the volumetric SiF₄ emission. More importantly, the process is stable with no variation in thickness, uniformity, etch rate, particle adders, or stress over a 75 wafer marathon.

INTRODUCTION

Human activity is increasing the concentration of infrared absorbing molecules in the atmosphere. There is concern that as the earth's atmosphere becomes increasingly opaque to infrared radiation, temperatures will increase i.e., global warming. In 1997 (Earth Summit, Kyoto, Japan¹), the Conference of the Parties agreed to limit emissions of global warming gases. Global warming gas emissions are primarily CO₂, however, perfluorocompounds (PFCs) used in semiconductor processing (e.g., CF₄, C₂F₆, C₃F₈, SF₆, NF₃) which have a high global warming potential² (GWP) due to their strong infrared absorbances and long lifetimes. While the semiconductor industry's contribution to global warming would be small compared to energy-related CO₂ emissions,³ PFC emissions should be minimized because of their persistence: PFCs will remain in the atmosphere for thousands of years after they are emitted.

This report describes the optimization of a C_2F_6 -based chamber clean for an Applied Materials' TEOS PECVD process. Optimization involves minimizing PFC process emissions while maintaining an acceptable clean time. Volumetric PFC emissions were determined by quadrupole mass spectrometry (QMS) and fourier transform infrared (FTIR) spectroscopy (Section 2). Clean times were determined by optical endpoint detection. The effluent from a baseline C_2F_6 chamber clean process is analyzed in section 3. This C_2F_6 -based chamber clean was optimized (Section 4) using a central composite design of experiments (DOE) methodology. Our strategy was to measure response surfaces for the PFC emissions (million metric tons carbon equivalent, MMTCE) and clean time as a function of C_2F_6 gas flow, $O_2:C_2F_6$ ratio, and pressure. From these response surfaces, clean processes were identified that result in both lower MMTCE values and shorter clean times. The PFC emission reductions and clean times predicted by the response surfaces are then verified through measurements on these optimized processes (Section 5). The optimized clean processes remove all of the TEOS residue from the PECVD chamber as indicated by the volumetric SiF_4 emission. Most importantly, the process is stable with no variation in thickness, uniformity, etch rate, particle adds, or stress over a 75 wafer mini-marathon. Qualification of the optimized C_2F_6 clean processes is described in Section 6.

2. EXPERIMENTAL METHODOLOGY

TEOS films (1.8 μm) were deposited in a 200 mm Applied Materials' Centura DxZ chamber. Measurements were made downstream of the process pump (Fig. 1) at ambient pressure using QMS and FTIR. The QMS instrument was used for C_2F_6 , CF_4 , SiF_4 , and F_2 determinations while the FTIR measured C_2F_6 , CF_4 , SiF_4 , and HF concentrations. There is excellent agreement between these two independent measurements of C_2F_6 and CF_4 concentrations. After each deposition the wafer was removed from the chamber and an *in situ* RF C_2F_6/O_2 plasma was used to clean the chamber. The baseline clean process is a timed etch. Throughout, the electrode spacing was kept fully open. After each experimental (DOE) clean process the PECVD chamber was cleaned using the baseline clean. This overetch ensures that all of the TEOS residue was removed before starting the next experimental clean. Clean times for the baseline and DOE processes were established from the optical end point monitor on the PECVD chamber using standard end-point criteria.

The process was sampled through a 1/4 inch VCR fitting at the exhaust of the process pump (Fig. 1). The sample inlet pressure was 725 torr throughout as measured by a capacitance manometer. Sample lines were 1/8 inch stainless steel tubing heat traced to ~ 100 °C. All sample lines were fluorine passivated by running the C_2F_6 plasma in a clean chamber until the F_2 concentration reached equilibrium (as measured by QMS).

2.1 QMS Measurements of C_2F_6 , CF_4 , SiF_4 , and F_2

The processes were monitored with a UTI Qualitrac QMS having a 300 amu mass filter. The sample inlet was differentially pumped for fast sampling of a slightly

subambient atmosphere i.e., the QMS response time must be much shorter than changes in the gas composition of each process step. The mass locations were determined using N_2 (7, 14, 28 amu) and C_2F_6 (119 and 69 amu).

The QMS instrument was calibrated on-site for C_2F_6 and CF_4 using 1 % gas standards. Five (5) point or better calibration curves were measured using dynamic dilution methods to generate concentrations $\leq 10,000$ ppm. Due to sensitivity changes, the QMS analyzer was calibrated each day. For CF_4 measurements using QMS, the contribution of C_2F_6 to the 69 amu signal was subtracted using the 69:119 amu cracking pattern. The C_2F_6 cracking pattern is obtained from the C_2F_6 calibration curve which was measured daily.

2.2 FTIR Measurements of C_2F_6 , CF_4 , SiF_4 , and HF

Concentrations were determined using a Midac I2000 FTIR spectrometer with a HgCdTe detector and a 0.01 m Axiom gas cell. Absorbance spectra were collected at 1 cm^{-1} resolution and signal averaged over 8 scans.

As for the QMS measurements, the FTIR instrument was directly calibrated on-site for C_2F_6 and CF_4 using 1 % gas standards and dynamic dilution methods. The infrared absorbance regions used for C_2F_6 and CF_4 quantitation are 1220-1275 cm^{-1} and 1270-1292 cm^{-1} , respectively. Since it was demonstrated that the C_2F_6 and CF_4 calibration curves are linear over the range of interest, concentrations were determined using a single point calibration (16.55 ppm.m for C_2F_6 measurements and 15.00 ppm.m for CF_4 measurements).

Absorbance in the region 992-1050 cm^{-1} was used as a monitor of the SiF_4 concentrations. The FTIR spectrometer was directly calibrated *ex situ* for SiF_4 measurement using a 1.0 % gas standard. These concentrations were determined from a single point calibration: reference spectrum 10.00 ppm.m.

2.3 Pump Purge Measurement

Because measurements are made downstream of the process pump, the process byproducts are diluted by the pump purge. It is important to know the total gas flow to determine volumetric emissions i.e. standard cubic centimeters (scc). The pump purge was determined by flowing C_2F_6 from the gas panel and measuring its concentration using the QMS which has been independently calibrated for C_2F_6 . The dilution factor (74,034 sccm) is obtained from the slope of C_2F_6 concentration versus C_2F_6 gas flow.

3. EMISSIONS FROM THE BASELINE C_2F_6 CHAMBER CLEAN PROCESS

The byproducts of the C_2F_6 clean are CF_4 , SiF_4 , F_2 , HF, and unutilized C_2F_6 . The concentrations of C_2F_6 and CF_4 measured by both QMS and FTIR are plotted in Fig. 2. There is excellent agreement (5 %) between these two independent measurements. There

is a sharp increase in the C₂F₆ concentration when the process gases are turned on. The initial CF₄ spike measured by QMS results from an under correction from the C₂F₆ signal (Section 2.1). Once the RF power is applied, the C₂F₆ concentration drops to 2100 ppm, reflecting utilization of the C₂F₆ gas. At end point, there is an increase in the CF₄ concentration to 1500 ppm and a greater decomposition of C₂F₆.

Volumetric emissions (Tables 1 and 2) are obtained by integrating under the gas flow profile (Fig. 2) and multiplying by the pump purge (Section 2.3). During the baseline clean (timed etch), the C₂F₆ and CF₄ emissions measured by QMS are 284 scc and 103 scc, respectively, for the 6 processed wafers. The C₂F₆ and CF₄ emissions measured by FTIR (275 scc and 116 scc, respectively) are in good agreement with the QMS result.

QMS	1	2	3	4	5	6	AVE±σ	g/wafer	MMTCE
C ₂ F ₆ (scc)	280	275	292	289	284	282	284±6	1.75	4.38E-09
CF ₄ (scc)	113	121	84	83	90	127	103±20	0.41	7.18E-10
Total MMTCE									5.10E-09

Table 1. Volumetric PFC emissions (QMS data) for the baseline clean (timed etch).

FTIR	1	2	3	4	5	6	7	AVE±σ	g/wafer	MMTCE
C ₂ F ₆ (scc)	277	273	276	275	271	276	276	275±2	1.69	4.25E-09
CF ₄ (scc)	117	114	117	117	116	117	117	116±1	0.46	8.09E-10
Total MMTCE										5.06E-09

Table 2. Volumetric PFC emissions (FTIR data) for the baseline clean (timed etch).

Process emissions on a g/wafer basis are calculated from the volumetric (scc) emissions using the molecular weight of C₂F₆ (138 amu) and CF₄ (87 amu). MMTCE values are used as a measure of environmental impact. The MMTCE value for the baseline clean process is 5.1×10⁻⁹ assuming a GWP of 9200 and 6500 for C₂F₆ and CF₄, respectively.

4. OPTIMIZATION OF THE C₂F₆ CLEAN PROCESS

The C₂F₆ clean process was optimized using a central composite design of experiments (DOE) methodology summarized in Table 3. This DOE sets alpha to 1 and includes 3 central point replicates (#1, #5, #6). The C₂F₆ flow rate (200 to 400 sccm), pressure (3.5 to 5.5 torr), and O₂:C₂F₆ ratio (1.4 to 2.0) was varied while measuring the responses clean time and PFC emissions (MMTCE value). RF power was fixed at 1500 W. Clean times were determined using the optical end-point monitor. Since there is

good agreement between the QMS and FTIR measurements, MMTCE values were calculated from the QMS emissions data.

The response surface for the clean time is shown in Fig. 3 as a function of C_2F_6 flow and $O_2:C_2F_6$ ratio (the pressure is fixed). Shorter clean times are favored by higher C_2F_6 flow rates and lower $O_2:C_2F_6$ ratios. The corresponding MMTCE response surface is shown in Fig. 4 (the pressure is fixed). Lower MMTCE values are favored by lower C_2F_6 flow rates and lower $O_2:C_2F_6$ ratios. These response surface show that faster cleans and lower PFC emissions are both favored by lower $O_2:C_2F_6$ ratios. PFC emissions reductions are possible therefore by reducing the C_2F_6 flow rates and maintaining an equivalent clean time by adjusting the O_2 concentration and pressure.

	C_2F_6 Flow (sccm)	$O_2:C_2F_6$ Ratio	Pressure (Torr)	Total Flow (sccm)	O_2 Flow (sccm)
1	300	1.7	4.5	810	510
2	300	1.4	4.5	720	420
3	200	2	5.5	600	400
4	400	1.7	4.5	1080	680
5	300	1.7	4.5	810	510
6	300	1.7	4.5	810	510
7	200	1.7	4.5	540	340
8	400	1.4	3.5	960	560
9	300	2	4.5	900	600
10	400	2	3.5	1200	800
11	200	2	3.5	600	400
12	400	1.4	5.5	960	560
13	300	1.7	5.5	810	510
14	400	2	5.5	1200	800
15	200	1.4	3.5	480	280
16	200	1.4	5.5	480	280
17	300	1.7	3.5	810	510

Table 3. Design of experiments (DOE) for C_2F_6 optimization.

While lower flows result in lower MMTCE values, we were concerned that lower flows and higher pressures may not completely clean the chamber i.e. the lowest C_2F_6 flows and highest pressures may result in an incomplete clean. Volumetric SiF_4 emissions are a good measure of whether all of the TEOS residue has been removed from the process chamber. If some TEOS residue remains in remote areas, then less SiF_4 will be emitted during the cleans. Relative SiF_4 emissions for all of the DOE processes are shown in Fig. 5 as a function of C_2F_6 flow and pressure. The quadrant at low C_2F_6 flows and high pressures result in less SiF_4 emission, indicating an incomplete clean. Optimized clean recipes were therefore limited to areas (Fig. 5) where the SiF_4 emissions are the same as that for the baseline clean process (i.e. relative SiF_4 emission of 1.00).

Note that for high flows and low pressures, more TEOS residue is removed (relative SiF₄ emissions >1.00) than the baseline clean process.

5. MMTCE VALUE AND CLEAN TIME FOR OPTIMIZED CLEAN PROCESS

The MMTCE and clean time response surfaces show that both the MMTCE values and clean times can be reduced by going to lower O₂:C₂F₆ ratios and higher pressure. To verify the MMTCE and clean time reduction, measurements were made on these actual processes. The chamber was cleaned using a timed etch. PFC emissions for this optimized process are 3.9×10⁻⁹ MMTCE while the clean time is reduced by 9 %. The power dependency (1500 to 2000 W) was also investigated (Fig. 6).

Volumetric emissions based upon the QMS measurements are summarized in Table 4 for the optimized and baseline processes. Volumetric emissions represent the average from 5 processed wafers. The clean time was determined by the optical endpoint monitor. Corresponding process emissions based upon the FTIR measurements are summarized in Table 5. Processes have been identified having lower PFC emissions with a faster clean time.

	Baseline Clean	Optimized C ₂ F ₆ Clean Process		
		(1500 W)	(1750 W)	(2000 W)
C ₂ F ₆ (scc)	268±8	199±3	162±6	146±4
CF ₄ (scc)	158±10	130±7	204±7	202±6
Clean Time Reduction	-	9 %	18 %	21 %
MMTCE (QMS) (timed etch)	5.2×10 ⁻⁹	3.9×10 ⁻⁹	3.9×10 ⁻⁹	3.7×10 ⁻⁹

Table 4. PFC emissions (volumetric and MMTCE) and clean time reduction for the optimized processes (QMS emissions data).

Note that the SiF₄ emissions for the optimized processes are identical to that for the baseline process (Fig. 7). This indicates that the optimized cleans effectively remove all of the TEOS residue from the process chamber. The lower MMTCE cleans remove an equivalent amount of SiF₄ as the baseline recipe, suggesting that these optimized processes completely clean the chamber. This conclusion is confirmed by process results from the marathon run (Section 6).

For the optimized 1750 W process, the MMTCE value has been reduced by 25 % (3.9×10⁻⁹) while the clean time is shortened by 18 %. For the optimized 2000 W process, the MMTCE value has been reduced by 29 % (3.7×10⁻⁹) while the clean time is shortened by 21 %.

	Baseline Clean	Optimized C ₂ F ₆ Clean Process		
		(1500 W)	(1750 W)	(2000 W)
C ₂ F ₆ (scc)	283±5	191±1	182±2	156±8
CF ₄ (scc)	119±2	127±1	174±2	182±4
Clean Time Reduction	-	9 %	18 %	21 %
MMTCE (FTIR) (timed etch)	5.2×10 ⁻⁹	4.0×10 ⁻⁹	4.0×10 ⁻⁹	3.7×10 ⁻⁹

Table 5. PFC emissions (volumetric and MMTCE) and clean time reduction for the optimized processes (FTIR emissions data).

6. QUALIFICATION OF THE OPTIMIZED C₂F₆ CLEAN

While volumetric SiF₄ emissions suggest that the optimized C₂F₆ clean removes all of the PECVD TEOS residue, it is necessary to confirm there is no long term process drift. Film thickness (Fig. 9), uniformity (Fig. 9), etch rate, particle adders, and stress were monitored during a 75 wafer qualification of the optimized clean process (1750 W). The process is stable. There is little variation of these metrics during the marathon and they do not trend.

7. SUMMARY

Clean processes were identified that result in both lower MMTCE values and shorter clean times. PFC emissions for the optimized C₂F₆ clean process have been reduced to 2.2×10⁻⁹ MMTCE (per μm PECVD TEOS deposition). This represents a 75 % reduction over typical clean processes for Applied Materials DxZ TEOS PECVD.^{4,5} Further emission reductions are possible through end point detection and exploring lower C₂F₆ flow rates, and lower O₂:C₂F₆ ratios. In addition to reducing PFC emissions, the optimized processes have faster clean times (9-18 %). Optimized cleans remove all of the TEOS residue from the PECVD chamber as indicated by the volumetric SiF₄ emission. Most importantly, the process has been qualified. There is no variation in thickness, uniformity, etch rate, particle adders, or stress over a 75 wafer marathon. Adjusting the process parameters so as to minimize PFC emissions from the C₂F₆ chamber clean is a viable strategy for installed PECVD equipment.

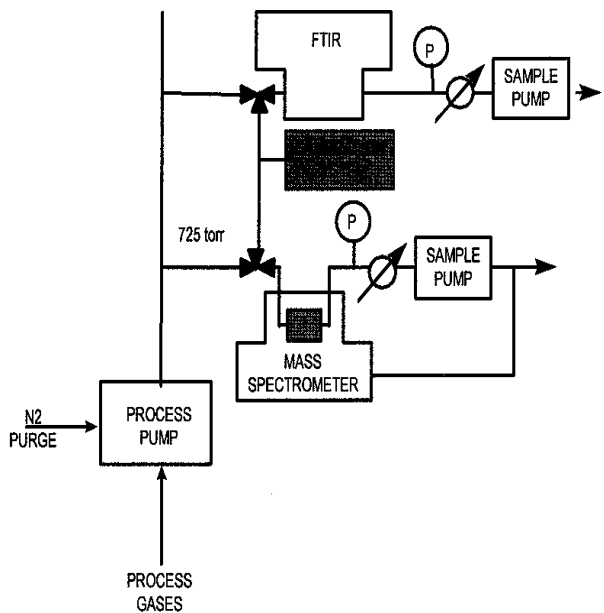


Figure 1. Schematic of analytical methodology used to quantify process effluents (QMS and FTIR).

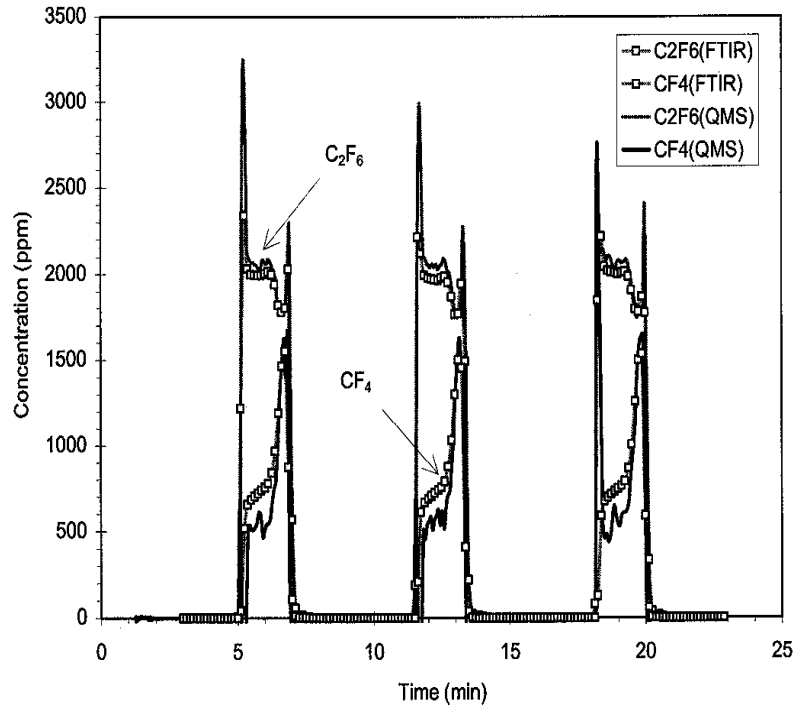


Figure 2. PFC emissions during Applied Materials' DxZ chamber clean. Concentrations were measured by both FTIR and QMS

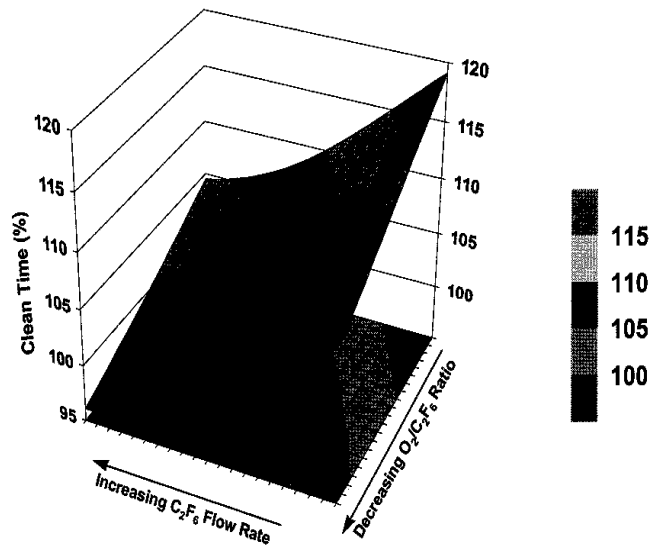


Figure 3. Clean-time response surface as a function of C₂F₆ flow rate and O₂:C₂F₆ ratio (Pressure is fixed).

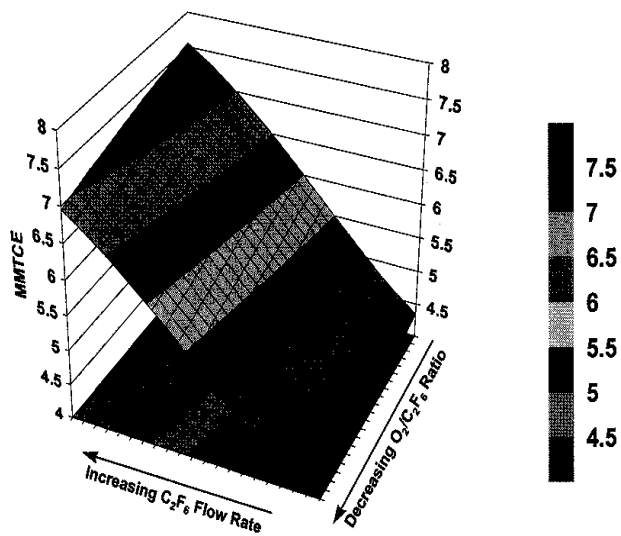


Figure 4. MMTCE response surface as a function of C₂F₆ flow rate and O₂:C₂F₆ ratio (Pressure is fixed).

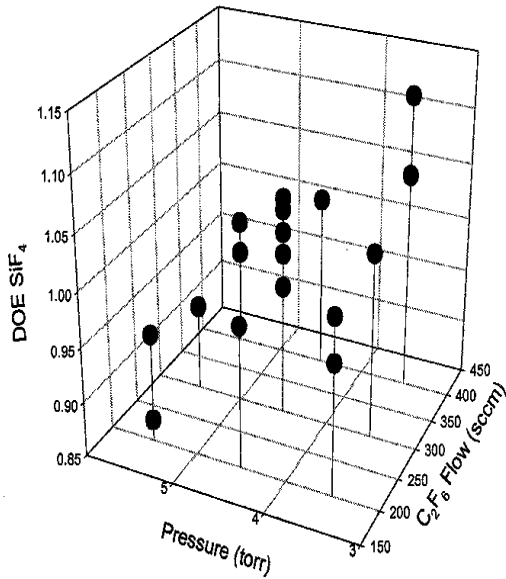


Figure 5. Volumetric SiF₄ emissions for the DOE clean processes.

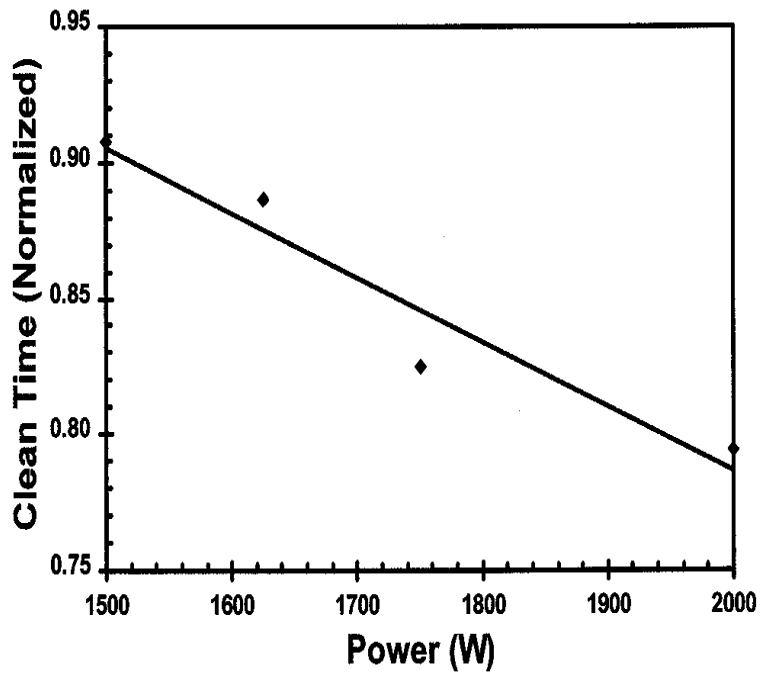


Figure 6. Power dependence of the optimized clean processes.

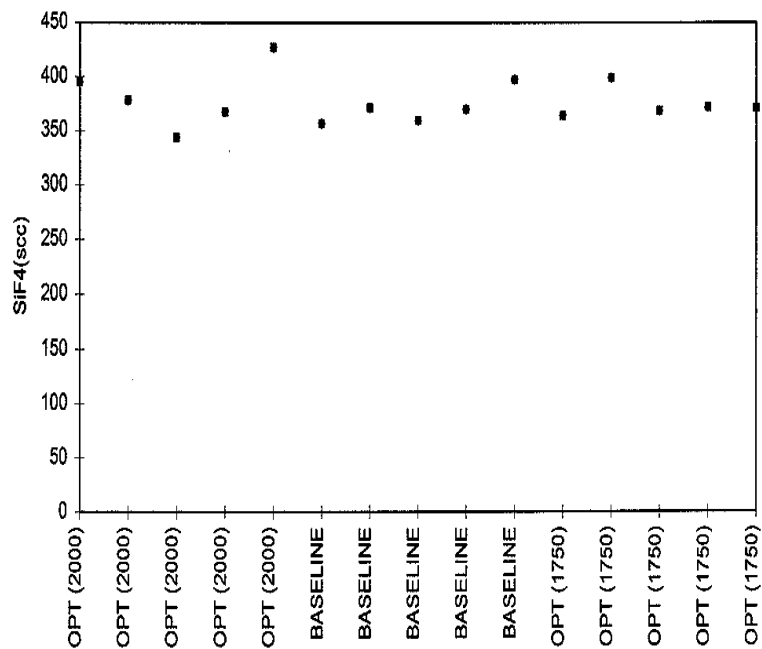


Figure 7. Volumetric SiF₄ emissions for the baseline and optimized processes.

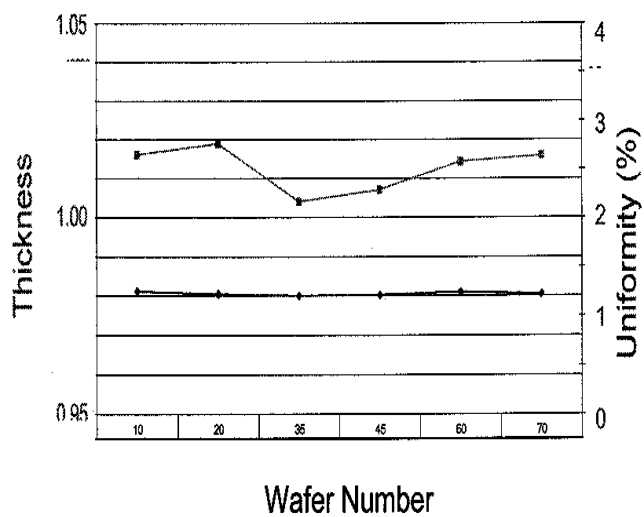


Figure 8. Variation in film thickness and uniformity during qualification of the optimized clean process.

REFERENCES

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- ¹ "Framework Convention on Climate Change," *Conference of the Parties, Kyoto, Japan*, December 1-10, 1997.
 - ² "Climate Change 1995," Intergovernmental Panel on Climate Change, Cambridge University Press.
 - ³ "PFCs and the Semiconductor Industry: A Closer Look," P. J. Maroulis, J. G. Langan, A. D. Johnson, R. G. Ridgeway, and H. P. Withers, *Semiconductor International*, November (1994).
 - ⁴ "Evaluation of Various NF₃ Clean Solutions for Applied Materials Dielectric CVD Equipment," L. Mendicino, S. Filipiak, B. Boeck, J. Chan, M. Tiemessen, A. Atherton, J. Langan, R. Pearce, A. Johnson, R. Ridgeway, and P. Maroulis, *SEMICON Southwest (1998): A Partnership for PFC Emissions Reductions*
 - ⁵ "Reducing Perfluorocarbon Gas Emissions from CVD Chamber Cleans: Protecting the Environment While Reducing Costs," A. D. Johnson, W. R. Entley, and P. J. Maroulis, *SEMiconductor Magazine (to be published)*.