

# OPTIMIZING A TUNGSTEN LPCVD CHAMBER CLEAN PROCESS: MINIMIZING PFC EMISSIONS WHILE REDUCING COSTS

Andrew D. Johnson, Christopher L. Hartz, and Peter J. Maroulis  
*Air Products and Chemicals, Inc.*

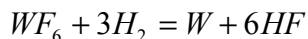
Wolfram Karcher, Kai-Uwe Reichow, Hubert Winzig, and Dieter Zeiler  
*Infineon Technologies AG*

Frank Weber, Josh Collins, and John Langan  
*Novellus Systems, Inc.*

PFC emissions associated with tungsten LPCVD were minimized for a Novellus Concept-2 Altus 200 mm process tool. Optimization involves minimizing PFC process emissions (MMTCE value) while maintaining a reasonable clean time. MMTCE and clean time response surface were measured as a function of C<sub>2</sub>F<sub>6</sub> gas flow, C<sub>2</sub>F<sub>6</sub> concentration, pressure, and RF power. Volumetric PFC emissions were measured in a production fab by both quadrupole mass spectrometry (QMS) and fourier transform infrared (FTIR) spectroscopy. Faster cleans are favored by higher C<sub>2</sub>F<sub>6</sub> flow rates, lower pressures and lower C<sub>2</sub>F<sub>6</sub> concentrations as well as higher RF-power. Lower PFC emissions are possible by using lower C<sub>2</sub>F<sub>6</sub> flow rates, lower C<sub>2</sub>F<sub>6</sub> concentrations, lower pressure and higher RF power. Processes having lower PFC emissions, by reducing the C<sub>2</sub>F<sub>6</sub> flow rate, maintain reasonable clean times by adjusting other process parameters such as pressure and concentration. In addition to reducing PFC emissions, C<sub>2</sub>F<sub>6</sub> process optimization can provide a considerable reduction in gas costs.

## 1. INTRODUCTION

Semiconductor devices are manufactured through the sequential deposition and patterning of thin film materials over a silicon substrate. Many of these materials (e.g., silicon oxide, silicon nitride, and tungsten) are deposited using chemical vapor deposition (CVD) techniques. For example, tungsten is deposited through the H<sub>2</sub> reduction of WF<sub>6</sub>:



Tungsten is deposited not only on the silicon wafer but also on the surfaces of the CVD chamber. Periodically, this tungsten residue needs to be removed by a chamber clean process. The chamber is cleaned by etching tungsten in a fluorine plasma to form WF<sub>6</sub>. Perfluorocompounds (PFCs, e.g. CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, NF<sub>3</sub>) are a convenient source of fluorine in CVD chamber clean processes because they are not corrosive. Since PFCs do not react with the materials of construction or atmospheric gases under ambient conditions, they are easy to handle.

The non-reactivity of PFCs which makes them attractive for chamber clean applications does, however cause environmental problems. The atmospheric lifetimes of PFCs are extremely long, e.g., 10,000 years for C<sub>2</sub>F<sub>6</sub>. PFCs that are emitted during CVD chamber cleaning will remain in the atmosphere for thousands of years. Since the atmospheric chemistry of PFCs is not completely known, emission of these gases should be minimized due to their persistence. In addition to being long lived, PFCs also absorb infrared radiation due to their fluorine bonding. Because of their strong infrared absorbances and long atmospheric lifetimes PFCs are suspected of contributing to global warming. Through the World Semiconductor Council (WSC) the global semiconductor industry has voluntarily committed to reduce its cumulative emissions of PFCs. IC manufacturers in the U.S., Europe, and Japan, have committed to

reducing PFC emissions to 90 % of 1995 levels by 2010. Industry growth projections imply that more substantial reductions for individual processes will be necessary to achieve this target level.

This paper describes the optimization of a C<sub>2</sub>F<sub>6</sub>-based chamber clean for an Novellus Concept-2 Altus (200-mm) process tool. Optimization involves minimizing PFC process emissions while maintaining a reasonable 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<sub>2</sub>F<sub>6</sub> chamber clean process is analyzed in section 3. This C<sub>2</sub>F<sub>6</sub>-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<sub>2</sub>F<sub>6</sub> gas flow, O<sub>2</sub>/C<sub>2</sub>F<sub>6</sub> ratio, pressure, and RF power. 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 were then verified through measurements on these optimized processes (Section 5). A number of clean processes are recommended depending upon specific FAB requirements: lower PFC emissions or shorter clean times. The chosen clean process is stable and will be qualified for production. Besides PFC reductions, these optimized clean processes also reduce gas costs due to lower flow rates and/or shorter clean times.

## 2. EXPERIMENTAL METHODOLOGY

Tungsten films (500 nm) were deposited using a Novellus Concept-2 Altus 200 mm process tool. After 25 depositions, corresponding to 2.1 μm cumulative thickness, an *in situ* RF C<sub>2</sub>F<sub>6</sub>/O<sub>2</sub> plasma was used to clean the chamber. The baseline clean is a one step process with end-point control. Effluent measurements were made downstream of the process pump (Fig. 1) at ambient pressure using quadrupole mass spectrometry (QMS) and fourier transform infrared spectroscopy (FTIR). Each experimental (DOE) clean process had a ~50 % overetch to ensure that all of the tungsten residue was removed before starting the next experimental clean. Clean times for the baseline and DOE processes were established from the F<sub>2</sub> emission profile measured by QMS.

The process was sampled through a ¼ 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<sub>2</sub>F<sub>6</sub> plasma in a clean chamber until the F<sub>2</sub> concentration reached equilibrium (as measured by QMS).

### 2.1 QMS Measurements

The processes were monitored with a UTI Qualitorr QMS having a 200 amu mass filter. Mass locations were determined using N<sub>2</sub> (7, 14, 28 amu) and C<sub>2</sub>F<sub>6</sub> (119 and 69 amu). The QMS instrument was calibrated on-site for C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> using gas standards (1 %). Five (5) point or better calibration curves were measured using dynamic dilution methods to generate concentrations ≤10,000 ppm. The sensitivity is obtained from the slope of the added concentration versus QMS response plot (Fig. 2). Due to sensitivity changes, the QMS analyzer was calibrated each day. For CF<sub>4</sub> measurements using QMS, the contribution of C<sub>2</sub>F<sub>6</sub> to the 69 amu signal was subtracted using the 69:119 amu cracking pattern obtained from the C<sub>2</sub>F<sub>6</sub> calibration curve.

### 2.2 FTIR Measurements

Concentrations were determined using a Midac Prospector FTIR spectrometer with a DTGS detector and a 0.01 m gas cell. Absorbance spectra were collected at 1 cm<sup>-1</sup> resolution and signal averaged over 4 scans. Similar to the QMS measurements, the FTIR instrument was directly calibrated on-site for

C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> using 1 % gas standards and dynamic dilution methods (Fig. 3). The infrared absorbance regions used for C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> quantitation are 1095-1135 cm<sup>-1</sup> and 1270-1290 cm<sup>-1</sup>, respectively.

### 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 rate to determine volumetric emissions i.e. standard cubic centimeters (scc). The pump purge was determined by flowing C<sub>2</sub>F<sub>6</sub> from the gas panel and measuring its concentration using the QMS which has been independently calibrated for C<sub>2</sub>F<sub>6</sub>. The dilution factor (74,034 sccm) is obtained from the slope of reciprocal C<sub>2</sub>F<sub>6</sub> concentration versus reciprocal C<sub>2</sub>F<sub>6</sub> gas flow.

### 2.4 Clean Time Measurements: QMS End Point Determination

Clean times are determined using the QMS. Fluorine F<sub>2</sub> emissions are monitored during the chamber clean at 38 amu and the clean time obtained from the concentration profile (Fig. 4). While the chamber is being cleaned, there is little F<sub>2</sub> emissions since fluorine is consumed by etching. As the CVD residue clears, however, the F<sub>2</sub> concentration increases. End point is defined as the time when the F<sub>2</sub> concentration reaches 95 % of its overetch value.

## 3. EMISSIONS FROM THE BASELINE C<sub>2</sub>F<sub>6</sub> CHAMBER CLEAN PROCESS

The baseline clean process uses C<sub>2</sub>F<sub>6</sub> (1300 sccm) and O<sub>2</sub> (1300 sccm) at a pressure of 0.43 torr and 2350 W RF power. The byproducts of the clean are CF<sub>4</sub>, WF<sub>6</sub>, WOF<sub>4</sub>, F<sub>2</sub>, HF, and unutilized C<sub>2</sub>F<sub>6</sub>. The concentrations of C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> measured by FTIR are plotted in Fig. 5. There is a sharp increase in the C<sub>2</sub>F<sub>6</sub> concentration when the process gases are turned on. Once the RF power is applied, the C<sub>2</sub>F<sub>6</sub> concentration drops to ~20,000 ppm, reflecting utilization of the C<sub>2</sub>F<sub>6</sub> gas. At end point, there is an increase in the CF<sub>4</sub> concentration to 5,000 ppm and a greater decomposition of C<sub>2</sub>F<sub>6</sub>.

Volumetric emissions (Table 1) are obtained by integrating under the gas flow profile (Fig. 5) and multiplying by the pump purge (Section 2.3). During the baseline clean, the C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> emissions are 13,460 scc and 2,530 scc, respectively. These PFC emissions correspond to 226×10<sup>-9</sup> MMTCE. The clean time measured from the F<sub>2</sub> concentration profile is 1017±29 s.

	1	2	3	4	5	6	AVE
C <sub>2</sub> F <sub>6</sub> (scc)	13,854	13,849	14,192	13,172	12,808	12,884	13,460±580
CF <sub>4</sub> (scc)	2,595	2,611	2,755	2,445	2,394	2,378	2,530±148

**Table 1.** Volumetric PFC emissions for the baseline C<sub>2</sub>F<sub>6</sub>/O<sub>2</sub> clean process.

## 4. OPTIMIZING THE C<sub>2</sub>F<sub>6</sub> CLEAN PROCESS: DESIGN OF EXPERIMENTS

The C<sub>2</sub>F<sub>6</sub> clean process was optimized using a central composite design of experiments (DOE) methodology. This DOE sets alpha to 1 and includes 3 central point replicates. The C<sub>2</sub>F<sub>6</sub> flow rate (800 to 1600 sccm), pressure (0.5 to 1.0 torr), C<sub>2</sub>F<sub>6</sub> concentration (45 to 60 %) and RF power (2000 to 4000 W) were varied while measuring the responses clean time and PFC emissions (MMTCE value). MMTCE values were calculated from the FTIR emissions data.

The response surface for the clean time is shown in Fig. 6 as a function of C<sub>2</sub>F<sub>6</sub> flow and C<sub>2</sub>F<sub>6</sub> concentration (the pressure and power are fixed). Shorter clean times are favored by higher C<sub>2</sub>F<sub>6</sub> flow rates and lower C<sub>2</sub>F<sub>6</sub> concentrations. Other response surfaces show that faster cleans are favored by lower pressures and higher RF powers. The corresponding MMTCE response surface is shown in Fig. 7 (the pressure and RF power is fixed). Lower MMTCE values are favored by lower C<sub>2</sub>F<sub>6</sub> flow rates and

lower C<sub>2</sub>F<sub>6</sub> concentrations. These response surface show that faster cleans and lower PFC emissions are both favored by lower C<sub>2</sub>F<sub>6</sub> concentrations and lower pressure. PFC emissions reductions are possible therefore by reducing the C<sub>2</sub>F<sub>6</sub> flow rates and maintaining an equivalent clean time by adjusting the C<sub>2</sub>F<sub>6</sub> concentration, pressure and RF power.

Examination of the response surfaces for clean time and PFC emissions allows a number of clean processes to be recommended. Depending on FAB needs, processes can be chosen that balance PFC emissions reduction with clean time. Recommended processes are summarized in Table 2.

	<b>Standard Infineon</b>	<b>Comparable Clean Time</b>	<b>Low MMTCE</b>	<b>High Power: Low MMTCE</b>	<b>High Power: Fast Clean</b>
C <sub>2</sub> F <sub>6</sub> (sccm)	1300	1100	850	800	1600
O <sub>2</sub> (sccm)	1300	1345	1040	980	1960
P (torr)	0.43	0.50	0.50	0.50	0.50
Power (W)	2350	2350	2350	3500	3500
Clean Time Change (%)	-	0 %	+10 %	-5 %	-24 %
MMTCE Change (%)	-	-22 %	-35 %	-50 %	-20 %

**Table 2.** Recommended processes from the DOE response surfaces.

Processes were identified that maintain the same clean time but reduce PFC emissions by 22 % (Comparable Clean Time). If a 10 % increase in clean time can be tolerated, then a 35 % PFC emissions reduction is possible (Low MMTCE). By using higher RF powers, more dramatic PFC emission reductions are possible while maintaining, or reducing, the clean time.

## 5. RECOMMENDED PROCESSES: VERIFYING PFC EMISSIONS AND CLEAN TIMES

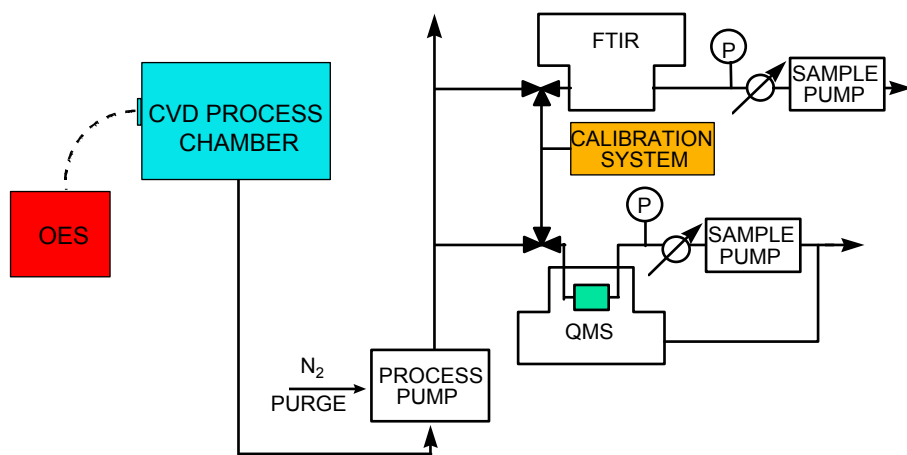
The clean time and MMTCE response surfaces allowed a number of clean processes to be recommended, depending upon fab requirements (Table 2). It is necessary to verify these predictions with measurements for these actual processes. The concentration profiles during some of the recommended cleans are shown in Fig. 8.

There is good agreement between the predictions of the response surfaces and the actual measurements of MMTCE values and clean times. Volumetric based emissions and clean times for each of the recommended processes are summarized in Table 3. Volumetric emissions represent the average from 3-4 clean processes. Clean processes were identified that reduce PFC emissions 18 % ( $186 \times 10^{-9}$  MMTCE) while maintaining the same clean time (Comparable Clean Time process). If a 12 % increase in the clean time is acceptable, then a 31 % ( $156 \times 10^{-9}$  MMTCE) reduction in PFC emissions is possible (Low MMTCE Clean process). Alternatively, by using higher RF powers, both lower PFC emissions ( $115 \times 10^{-9}$  and  $187 \times 10^{-9}$  MMTCE) and shorter clean are possible (High Power Low MMTCE and High Power Fast Clean processes, respectively).

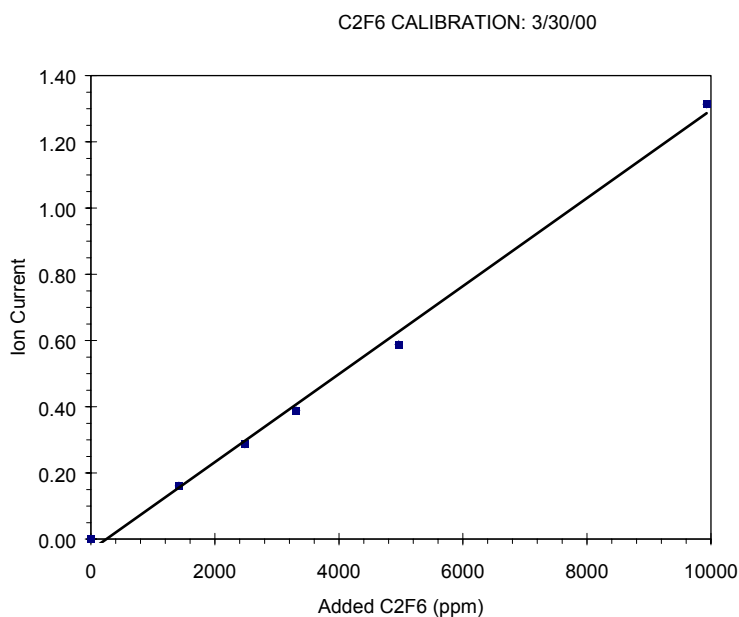
	<b>Standard Infineon</b>	<b>Comparable Clean Time</b>	<b>Low MMTCE</b>	<b>High Power: Low MMTCE</b>	<b>High Power: Fast Clean</b>
--	--------------------------	------------------------------	------------------	------------------------------	-------------------------------

C <sub>2</sub> F <sub>6</sub> (scc)	13,460	11,094	9,112	6,484	11,190
CF <sub>4</sub> (scc)	2,530	2,037	2,198	2,156	1,946
Predicted Clean Time (Change %)	1050 s	1050 s (0 %)	1150 s (+10 %)	1000 s (-5 %)	800 s (-24 %)
Measured Clean Time (Change %)	1017±29 s	1016±20 s (0 %)	1137±22 s (+12 %)	958±46 s (-6%)	758±38 s (-25 %)
Predicted MMTCE (×10 <sup>-9</sup> ) (Change %)	200	155 (-22 %)	130 (-35 %)	100 (-50 %)	160 (-20 %)
Measured MMTCE (×10 <sup>-9</sup> ) (Change %)	226±10	186±3 (-18 %)	156±3 (-31 %)	115±5 (-49 %)	187±10 (-17 %)

**Table 3.** Summary of PFC emissions and clean times for the recommended clean processes.

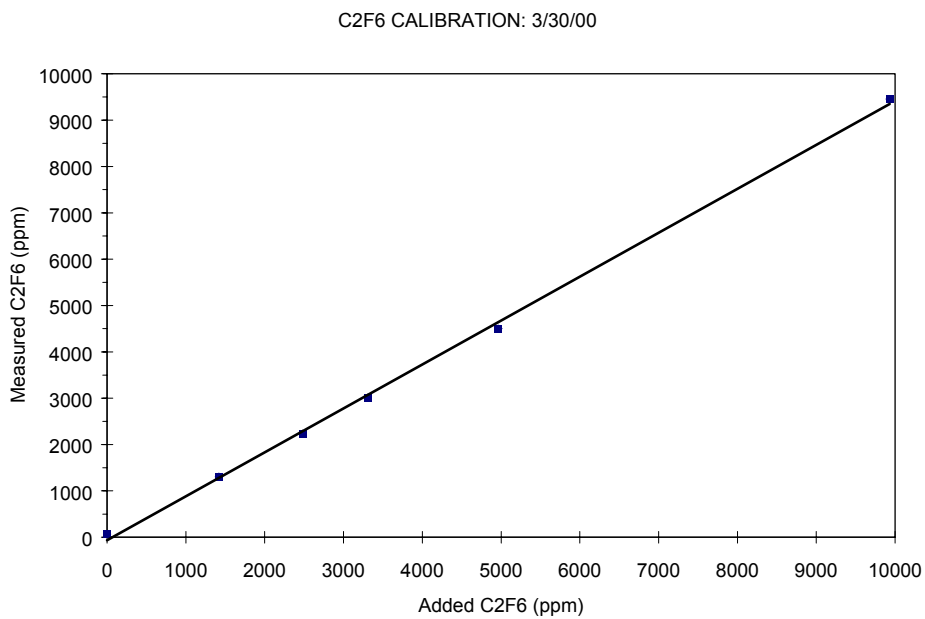


**Figure 1.** Schematic of analytical methodology used to quantify process effluents (QMS and (FTIR).



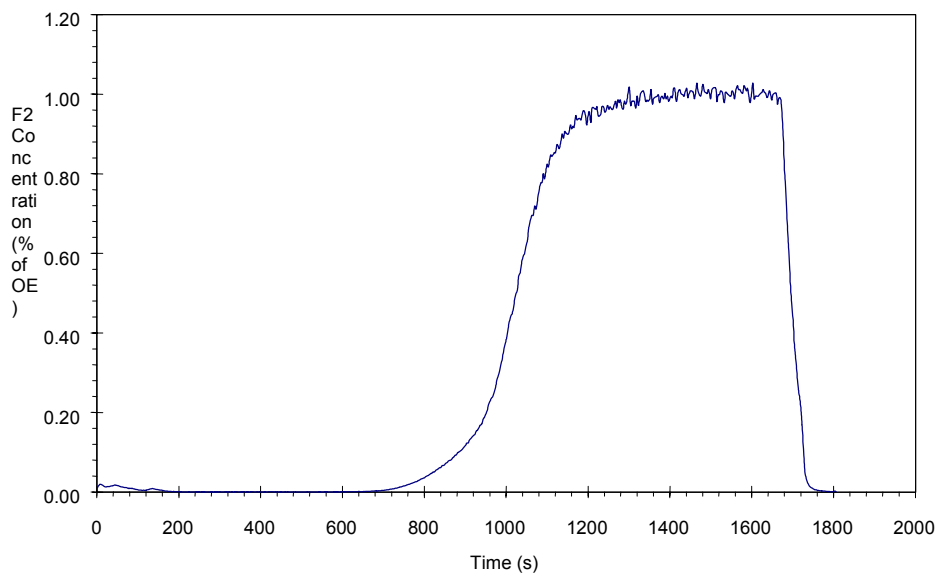
<i>Regression Statistics</i>	
Multiple R	0.998242
R Square	0.996488
Adjusted R	0.99561
Standard E	231.3144
Observatio	6
ANOVA	
	<i>df</i>
Regressor	1
Residual	4
Total	5
<i>Coefficients</i>	
Intercept	262.9603
X Variable	7496.45

**Figure 2.** QMS calibration data for C<sub>2</sub>F<sub>6</sub> concentrations.

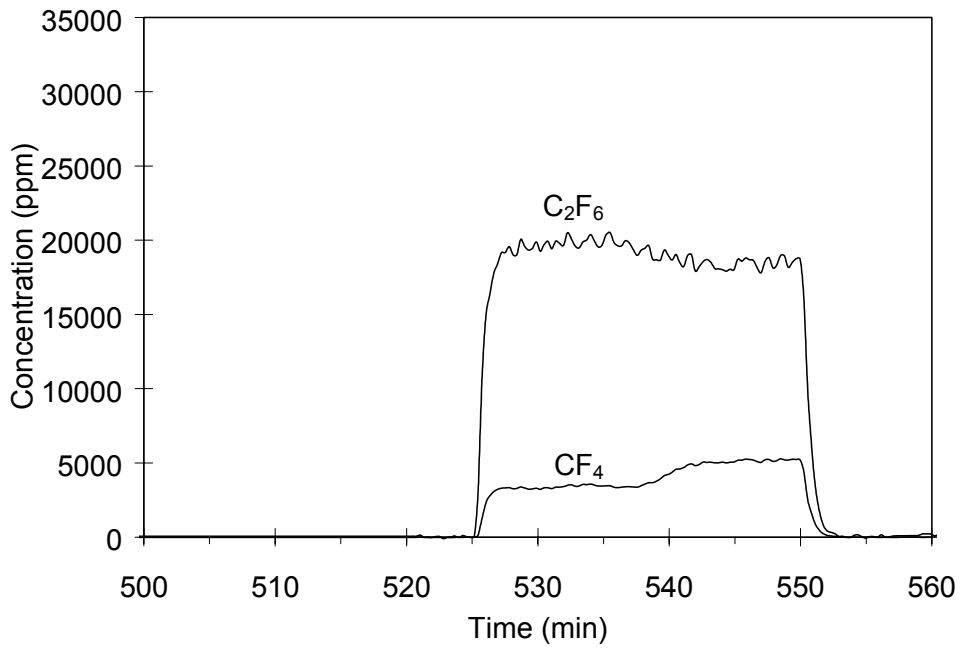


<i>Regression Statistics</i>	
Multiple R	0.999502
R Square	0.999003
Adjusted R	0.998754
Standard E	123.2287
Observatio	6
<i>ANOVA</i>	
	<i>df</i>
Regressor	1
Residual	4
Total	5
<i>Coefficients</i>	
Intercept	70.48721
X Variable	1.053613

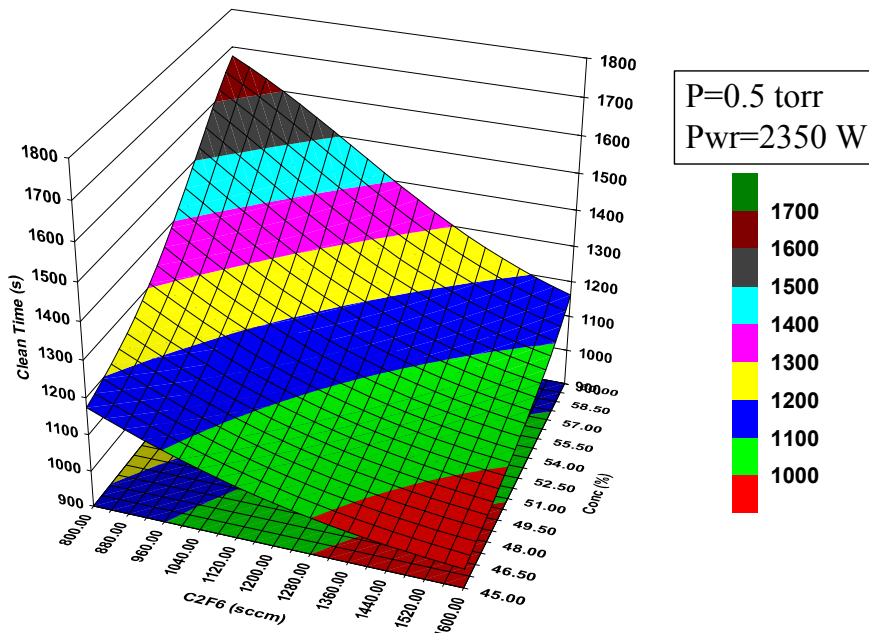
**Figure 3.** FTIR calibration data for C<sub>2</sub>F<sub>6</sub> concentrations.



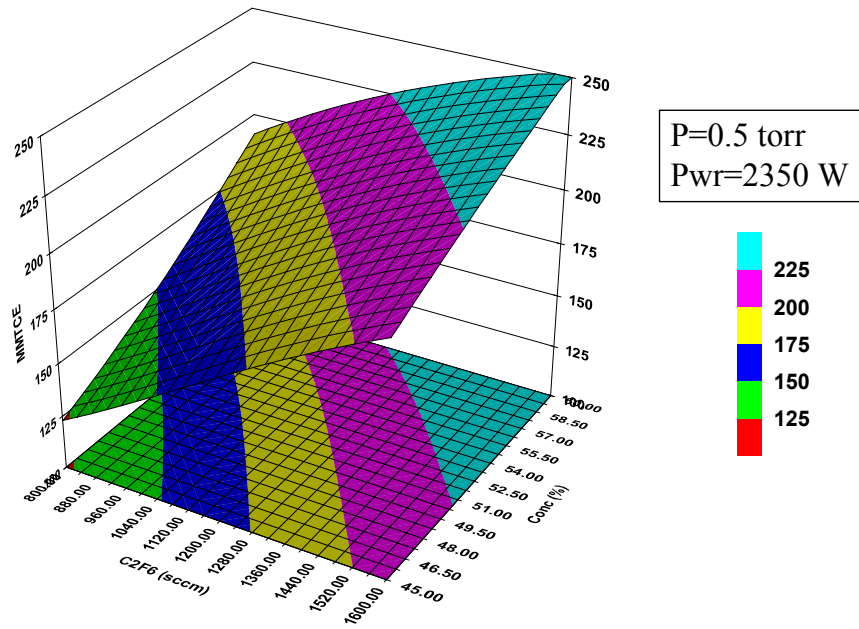
**Figure 4.** F<sub>2</sub> concentration during the chamber clean. End point is defined as the time when the F<sub>2</sub> concentration reaches 95 % of its overetch value.



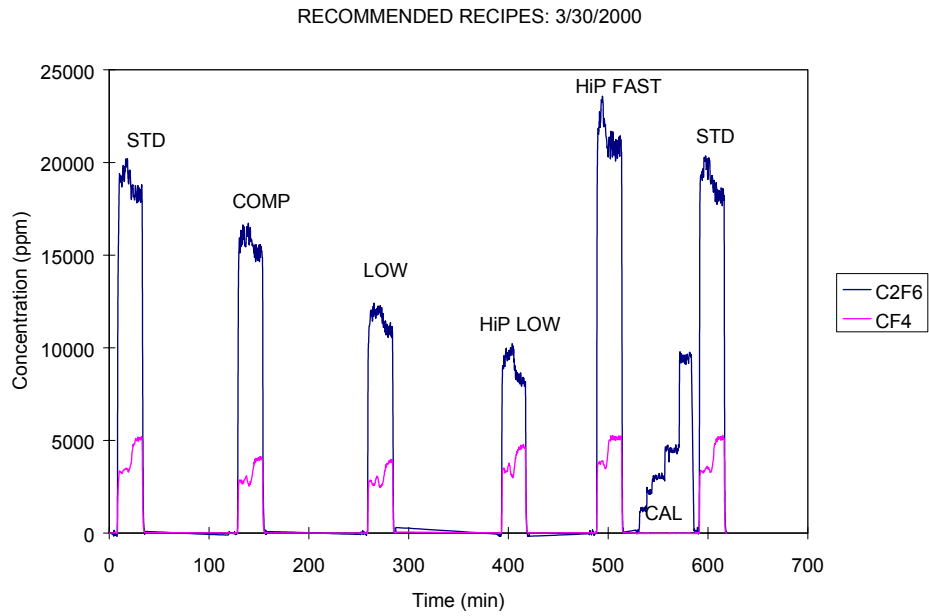
**Figure 5.** Concentration of C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> during baseline clean process.



**Figure 6.** Clean time response surface.



**Figure 7.** MMTCE response surface.



**Figure 8.** C<sub>2</sub>F<sub>6</sub> and CF<sub>4</sub> concentration profiles during the recommended clean processes