Motorola Evaluation of the Applied Science and Technology, Inc. (ASTeX) ASTRON Technology for Perfluorocompound (PFC) Emissions Reductions on the Applied Materials DxL Chemical Vapor Deposition (CVD) Chamber

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Abstract: The report presents the results of a study to demonstrate that the Applied Science and Technology, Inc. (ASTeX) ASTRON atomic fluorine generator can be effectively retrofitted onto installed Applied Materials 200 mm DxL chambers (lamp heated) to provide an improved chamber clean following the plasma-enhanced TEOS oxide deposition. Emissions were characterized to verify that high NF_3 utilization efficiencies and shorter clean times (relative to the baseline in situ C_2F_6 clean) could be obtained. A designed experiment was then conducted to determine the effects of NF_3 and argon flow and chamber pressure on the clean endpoint time and NF_3 utilization efficiency. Both quadrupole mass spectroscopy (QMS) and Fourier transform infrared (FTIR) spectroscopy were used to quantify the major fluorinated species to complete a fluorine balance around the ASTRON clean process.

Keywords: Chamber Cleaning, Chemical Vapor Deposition, Design of Experiments, Emissions Reduction, Fourier Transform Infrared Spectroscopy, Marathon Runs, Perfluorocompounds, TEOS

Authors: Laura Mendicino, Paul Thomas Brown, Stan Filipiak, and Laurie Beu (Motorola); Andrew D. Johnson, Richard V. Pearce, and Peter J. Maroulis (Air Products and Chemicals, Inc.); and Robert Basnett and William Holber (Applied Science and Technology, Inc.)

Approvals: Walter Worth, Program Manager
Bob Duffin, Director
Laurie Modrey, Technical Information Transfer Team Leader

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1 EXECUTIVE SUMMARY

To determine if the Applied Science and Technology, Inc. (ASTeX) ASTRON atomic fluorine generator is an effective remote plasma chamber cleaning technology, Motorola conducted an evaluation on an Applied Materials DxL chamber. Both quadrupole mass spectrometry (QMS) and Fourier transform infrared (FTIR) spectroscopy were used to quantify the major fluorinated gases in the process effluent. Process impact was determined by clean times, particle generation, and film thickness uniformity in the tool.

The ASTeX ASTRON was shown to be effective for 200 mm Applied Materials DxL (lamp heated) TEOS chamber cleaning. Throughout a 1000-wafer marathon of 2 µm plasma-enhanced TEOS (PETEOS) film depositions, no negative effects on film properties were noted. There was no evidence of particle generation. Process chamber clean times were 30–50% faster than the baseline C_2F_6 clean for PETEOS films.

The NF_3 utilization of the ASTRON has been demonstrated to be greater than 99% at all process conditions, thus effectively eliminating perfluorocompound (PFC) emissions from the chamber cleaning process. The volumetric emissions (NF_3, SiF_4, F_2, and HF) have been quantified and a fluorine balance of 100% or greater achieved. For a 0.5 µm film, the total amount of F_2 emitted when the clean was operated to endpoint (60 sec.) with 1000 sccm of NF_3 flow was 815 standard cubic centimeters (scc). This amount would be significantly reduced if the NF_3 flow was reduced and/or if the clean process was run only long enough to clean the process chamber (41 sec. for 0.5 µm film with 1000 sccm of NF_3 flow).

The results of the design of experiments (DOE) indicate that the NF_3 flow can be reduced by half—from 1000 sccm to 500 sccm—with no significant increase in endpoint time; the time to endpoint increased by only 9 sec. for a 1 µm film with this flow decrease (pressure = 2.1 Torr, Ar:NF_3 = 1:1). Endpoint times are shorter at lower chamber pressure. The endpoint time can also be reduced by increasing the Ar:NF_3 ratio. Although further characterization work should be done, the optimum process conditions with respect to clean time, gas flows, and total emissions would likely be an NF_3 flow of 500 sccm (reduced F_2 emissions and input gas cost without significant impact on clean time) with a pressure of 2.1 Torr (or throttle valve open) and an Ar:NF_3 ratio >1 (to reduce clean time).

A post-marathon and DOE inspection of the chamber yielded no observable damage to the internal components. The chamber body was clean bare aluminum with no observed defects. The chamber actually looked cleaner than pre-ASTRON installation. With the modified hardware, the combined total of both the clean optimization and marathon was greater than 3500 wafers.

2 INTRODUCTION

The *National Technology Roadmap for Semiconductors* (1997) calls for proactive reduction of emissions that may cause global climate change. Reducing emissions that contribute to global warming will continue as an important technology challenge as the roadmap becomes an international document in 1999. Perfluorocompounds, such as CF_4, C_2F_6, SF_6, and NF_3, are anthropogenic gases currently used in semiconductor manufacturing for chemical vapor deposition (CVD) chamber cleaning and plasma etching. All of SEMATECH's member companies have signed voluntary agreements to endeavor to reduce PFC emissions. It is expected that an international PFC emissions reduction goal will be set in 1999.

It has been determined that CVD chamber cleaning contributes up to 90% of the PFC emissions from a modern 200 mm fab producing multi-level metal devices. The concern over the fate of atmospherically persistent PFCs and the need to address industry calls for reduced PFC emissions have motivated the development of new chamber cleaning technologies. In a previous evaluation program at Motorola, Applied Materials demonstrated that remote plasma cleaning with NF_3 is a viable alternative to the in situ radio frequency (RF) C_2F_6 clean for the Applied DxZ chambers. Their remote microwave technology (known as µClean) demonstrated reduced clean times and NF_3 utilization efficiencies >90% with no negative effects on the deposition process. Because the µClean technology was developed for DxZ chambers only, a remote plasma cleaning solution was sought for the large installed base of Applied Materials 200 mm DxL (lamp heated) chambers.

ASTeX, a supplier of microwave plasma sources, ozone generators, and other components to semiconductor equipment manufacturers, has developed an atomic fluorine generator known as ASTRON. The ASTRON is a compact, self-contained, lid-mounted unit that uses a low-field toroidal (LFT) plasma to dissociate NF_3 (in argon [Ar]) to generate free fluorine. The gases are directed into the chamber where the free fluorine cleans the film deposits, such as silicon dioxide, polysilicon, and others. High NF_3 utilization efficiencies have been demonstrated by ASTeX in laboratory applications. To determine if the ASTRON is an effective remote plasma chamber cleaning technology, Motorola conducted an evaluation on an Applied Materials DxL chamber.

3 PROJECT OVERVIEW/BACKGROUND

The purpose of this study was to demonstrate that the ASTeX ASTRON atomic fluorine generator can be effectively retrofitted onto installed Applied Materials 200 mm DxL chambers (lamp heated) to provide an improved chamber clean following the plasma-enhanced TEOS oxide deposition. Emissions were characterized to verify that high NF_3 utilization efficiencies and shorter clean times (relative to the baseline in situ C_2F_6 clean) could be obtained. A designed experiment was then conducted to determine the effects of NF_3 and Ar flow and chamber pressure on the clean endpoint time and NF_3 utilization efficiency. Both QMS and FTIR were used to quantify the major fluorinated species to complete a fluorine balance around the ASTRON clean process.

4 EXPERIMENTAL DATA

4.1 Test Method Overview

The first phase of the study was a 1000-wafer marathon of 2 µm PETEOS oxide depositions followed by the baseline ASTRON clean using NF_3 and Ar as determined by ASTeX in a pre-marathon activity. The following data was collected during the marathon:

- Particle count performance
- Film thickness and uniformity
- Film stress and refractive index (RI)

Once the marathon was completed, Air Products performed a complete emissions characterization and fluorine mass balance for the ASTRON clean process for a 0.5 µm film deposition. A designed experiment was then conducted to determine the effect of pressure, NF_3 flow, and Ar flow on endpoint time and NF_3 utilization efficiency.

4.2 Equipment Information

The ASTRON AX7650 unit is a compact atomic fluorine generator that packages together a plasma source, power supply, and control system. The ASTRON device uses a LFT plasma to efficiently dissociate NF_3 (with Ar) over a wide range of operating conditions. Because of the small size of the ASTRON unit, it could be mounted directly on the lid of the DxL chamber. This mounting is illustrated in Figure 1. Only minor modifications to the DxL chamber were required:

- The gas mixing block was modified to allow the stream of dissociated gas from the ASTRON to enter the chamber.
- The sheet metal cover to the chamber was modified to allow for ASTRON mounting.
- The quartz tubes that are part of the constant voltage gradient feed-through, isolating the gas lines from the RF, were replaced with sapphire tubes of the same dimension.
- The quartz window at the bottom of the chamber that allows the light from the lamps into the chamber was replaced by a sapphire-coated quartz window of the same dimension.

A custom electronic interface was used to allow the ASTRON unit to be addressed by the P5000 system software as if it were a mass flow controller. This allowed the system to operate with only a new chamber clean recipe but no software changes to the P5000. QMS was used to monitor NF_3, F_2, and SiF_4 concentrations, whereas FTIR spectroscopy was used for hydrofluoric acid (HF) measurements. Measurements were made downstream of the process pump at ambient pressure using QMS and FTIR.

Wafers were processed in a 200 mm Applied Materials DxL (lamp heated) chamber on a P5000 mainframe. A Tencor 6100 analyzed particles using particle monitor wafers with a 2.5K Å film thickness. Film thickness, uniformity, and refractive index were measured on a Prometrix UV1250 using a 5 mm edge exclusion. Film stress was measured on a Tencor Flexus 5200h.

4.2.1 Pre-Marathon Experiments

Before the start of the marathon, an extensive set of experiments was conducted to determine the approximate optimum operating regime for the clean and the required clean time. Each experiment consisted of a 100-wafer deposition/clean cycle: a 1 µm deposition of SiO_2 followed by a clean cycle with a given set of clean conditions and a given clean time. After the 100-wafer run, the process chamber was opened and the inside examined to determine if any deposits had accumulated. If no deposits had occurred, the experiment was repeated with a shorter clean time. If deposits had occurred, the experiment was repeated with a longer clean time. This methodology allowed the required clean time for a 1 µm deposit at a given clean condition to be bracketed.

The pre-marathon experiments determined the marathon clean recipe for the 1 µm depositions. Using gas flows consisting of 1 standard liters per minute (slm) NF_3 and 1 slm Ar, the clean time for a 1 µm deposition was determined to be 64 sec. or less (clean time includes all steps associated with the clean recipe; NF_3 does not flow the entire time). Other SiO_2 thicknesses were run, and clean times associated with the 64 sec/µm baseline were verified.

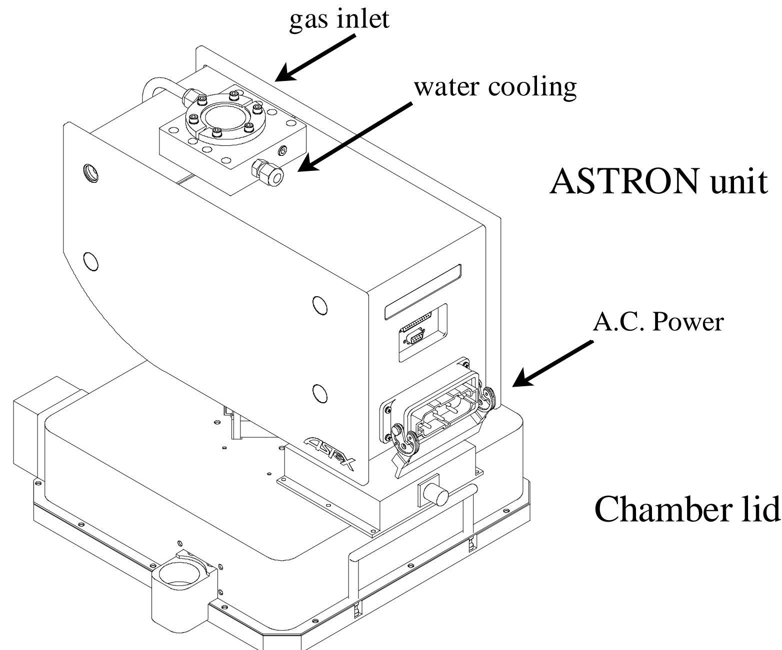


Figure 1 Isometric Drawing of the ASTRON Mounted on the Chamber Lid

Because the DxL chamber used for this study has been in use for several years, it had substantial deposits in areas inaccessible to the standard in situ plasma clean. This included the area behind the showerhead and blockerplate assemblies. After several hours of ASTRON operation, these areas were completely cleared of deposits.

As part of the pre-marathon activity, a short study was done to assess the feasibility of running the chamber RF clean simultaneously with the remote clean. The purpose of this was twofold:

- To increase the cleaning rate
- To provide an optical emission signal that can be used to endpoint the process

The results were positive, showing both reduced clean time and an endpoint signal.

4.2.2 Marathon Results

The 1000-wafer marathon was conducted using blanket test wafers and particle monitors. Cassettes of 25 wafers were run through the plasma enhanced chemical vapor deposition (PECVD) TEOS deposition process with an ASTRON clean between each wafer. The test wafer matrix is illustrated in Table 1. Three particle monitors at a film thickness of 2.5K Å were run. Film thickness and uniformity were measured on five wafers of varying thickness: 1K Å, 4K Å, 6K Å, and 10K Å. Stress and RI were measured on two wafers at 4K Å film thickness. This matrix was repeated for each cassette of 25 wafers throughout the marathon.

Table 1 Marathon Test Matrix

Wafer #	Film type	Thickness (Å)	Particles	Stress	RI	Thickness	Uniformity
1	blanket	20K					
2	particle	2.5K	X				
3	blanket	20K					
4	stress/RI	4K		X	X	X	X
5	blanket	20K					
6	blanket	20K					
7	blanket	20K					
8	blanket	20K					
9	blanket	20K					
10	blanket	20K					
11	blanket	20K					
12	blanket	20K					
13	blanket	20K					
14	blanket	20K					
15	particle	2.5K	X				
16	blanket	20K					
17	blanket	20K					
18	bright light	20K					
19	blanket	20K					
20	stress/RI	4K		X	X	X	X
21	thickness	10K				X	X
22	thickness	1K				X	X
23	thickness	6K				X	X
24	blanket	20K					
25	particle	2.5K	X				

Table 2 presents the clean times for the various film thicknesses. Both the NF_3 and Ar flows were set at 1.0 slm. Also shown are the baseline C_2F_6 in situ RF clean times for two PETEOS film thicknesses for comparison. The clean times included setup steps as well as the NF_3/Ar clean step. Note that the ASTRON clean times are 30–50% faster than the baseline C_2F_6 clean for the same PETEOS film thickness.

Table 2 ASTRON Marathon and Baseline C_2F_6 Clean Times

Film Thickness (Å)	ASTRON Clean Time (sec)	C_2F_6 Clean Time (sec)
1K	23	
2.5K	30	
4K	37	53
6K	46	
10K	64	
20K	109	212

Particle measurements for the 1000-wafer test are presented in Figure 2. Three particle monitors were included in each run of 25 wafers. The initial runs had some particle measurements greater than the acceptable level of 22 adders. This was attributed to some residual wafer chips from a broken wafer in the wafer handler. The particles were within specification after 300 wafers were processed. The three outlying measurements after wafer 700 were processed in the same cassette of 25 wafers; they were most likely caused by residue in the cassette contaminating the particle monitors. The particle data indicate that the ASTRON unit was able to completely clear the residue in the chamber after each wafer, thus preventing particle build-up. The clean times are, therefore, sufficient for each of the film thicknesses. The data also indicate that the ASTRON unit itself does not cause particle generation during normal operation.

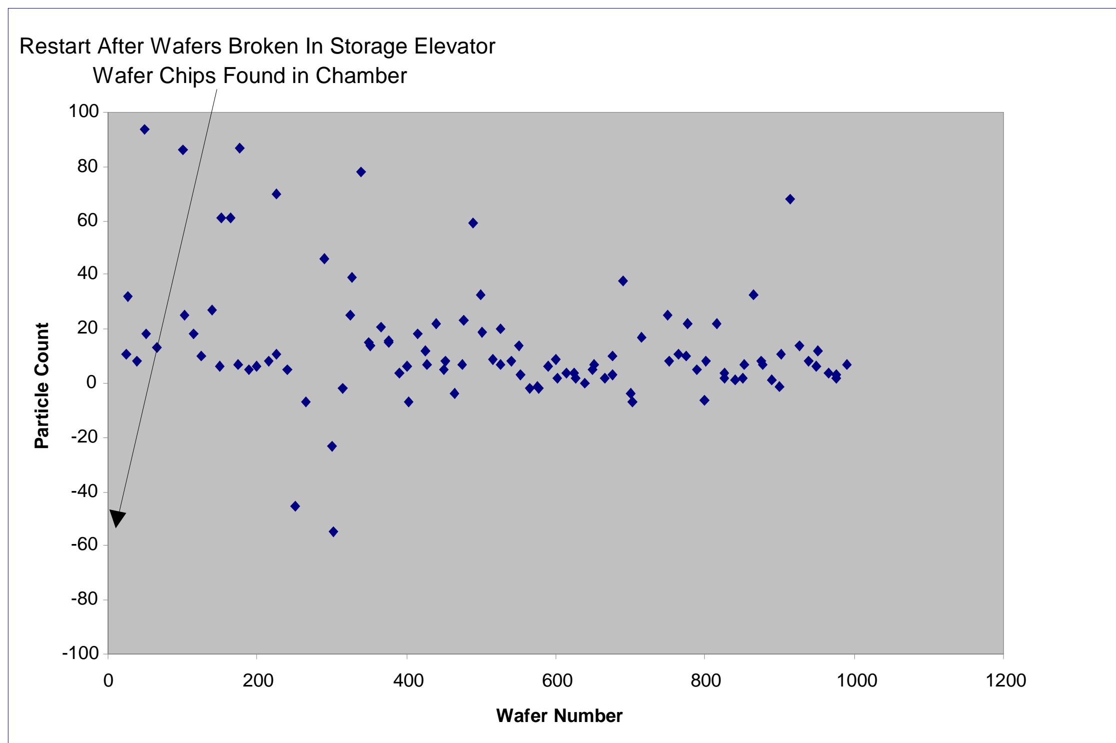


Figure 2 Particle Data for the 1000-Wafer Test Run

Figure 3 through Figure 6 present the film thickness and uniformity data for the four different film thicknesses routinely used for such measurements: 1K Å, 4K Å, 6K Å, and 10K Å. The film thicknesses throughout the test were within the normal range, always slightly higher than the nominal deposition thickness. There was also no significant variability (gradual increase or decrease) in actual thickness over the 1000 wafers. The film thickness uniformity was also within the acceptable range at approximately 1.0–1.5% for all four thicknesses. As with thickness, there was no noticeable variability in the uniformity over the 1000 wafers. This indicates that the ASTRON clean did not affect the deposition process with respect to these film properties.

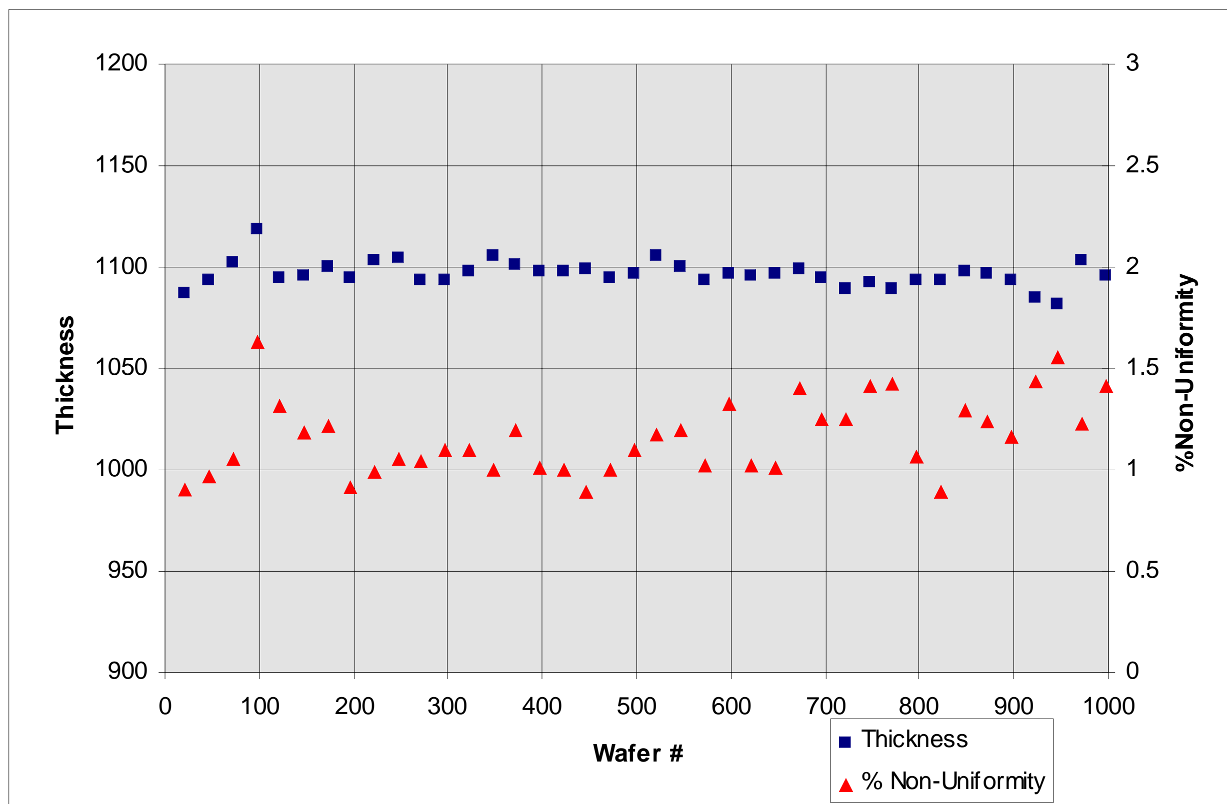


Figure 3 Film Thickness and Uniformity Data for a 1K Å Film

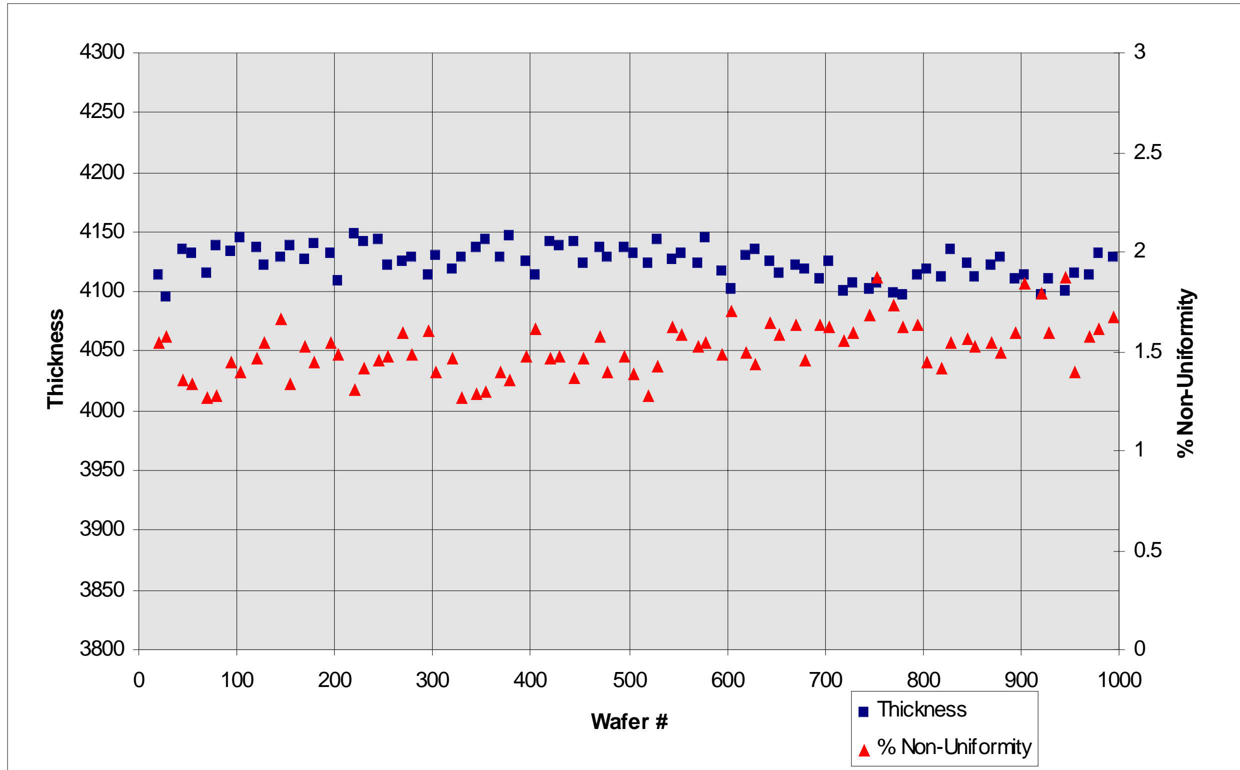


Figure 4 Film Thickness and Uniformity Data for a 4K Å Film

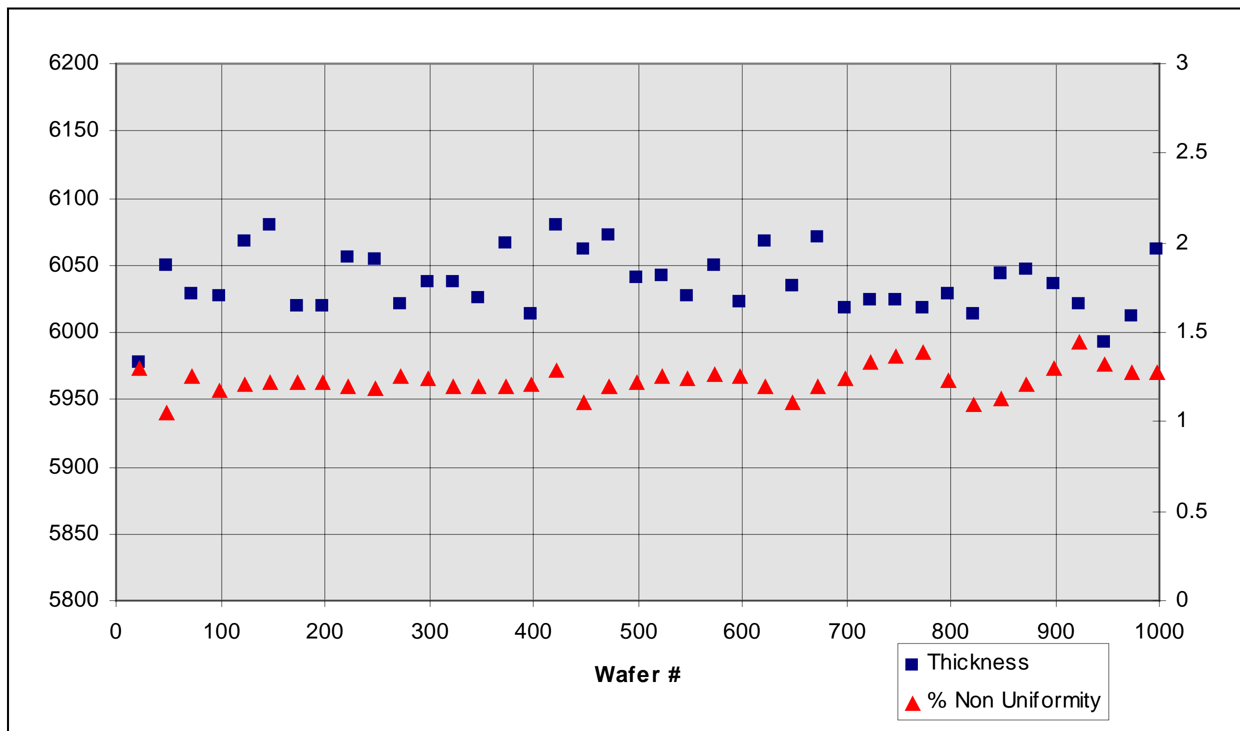


Figure 5 Film Thickness and Uniformity Data for a 6K Å Film

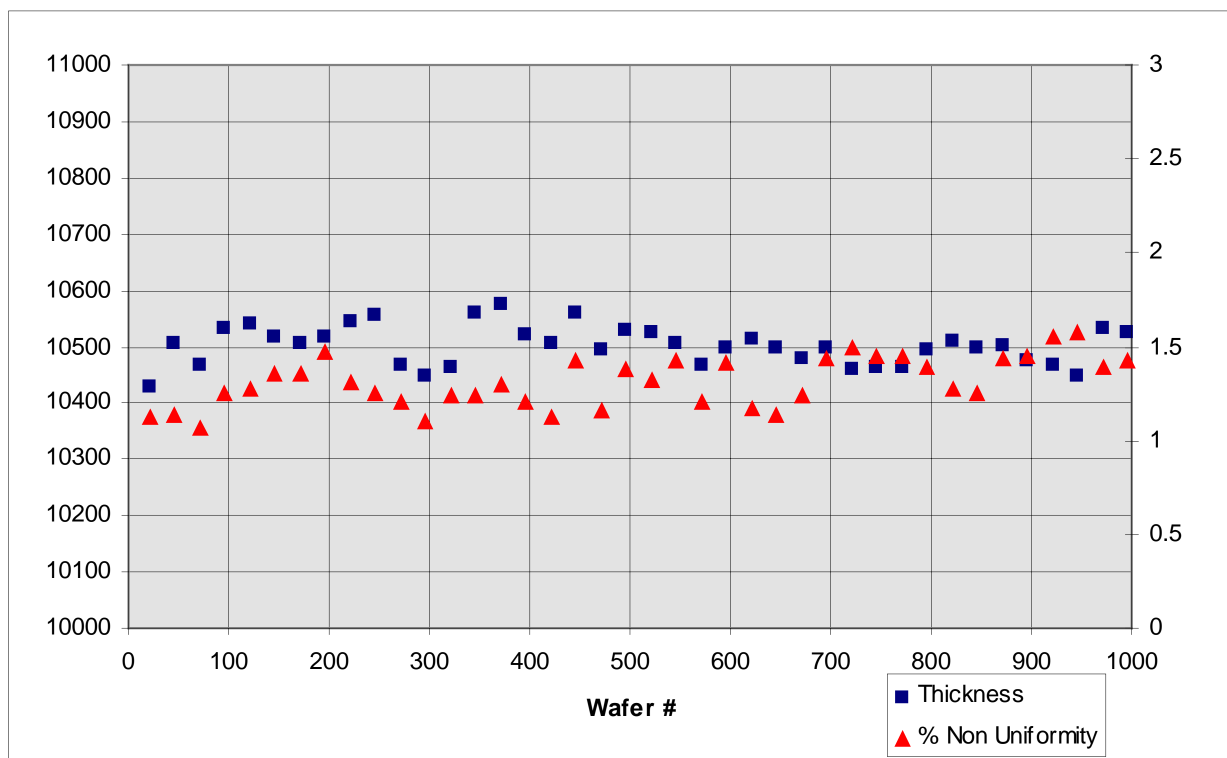


Figure 6 Film Thickness and Uniformity Data for a 10K Å Film

The film stress and refractive index measurements are shown in Figure 7. As with the other film parameters, these are within the acceptable range. The film stress was approximately -140 MPa throughout the marathon. The refractive index was also constant at 1.455. Again, the ASTRON clean did not affect the deposition process with respect to these film properties.

Based on the results of the 1000 wafer marathon, it can be concluded that the ASTRON clean does not have any negative effect on the plasma-enhanced TEOS oxide deposition process, as indicated by the film properties, and does not cause particle generation during normal operation.

4.3 Emissions Characterization Results

4.3.1 Instrumentation and Calibration

4.3.1.1 QMS Measurements of NF_3, SiF_4, and F_2

The processes were monitored with a UTI Qualitrace QMS having a 200 atomic mass unit (amu) mass filter. The QMS features a closed ion source for high pressure process analysis. The sample inlet was differentially pumped to quickly sample a slightly sub-ambient atmosphere (i.e., the QMS response time must be much shorter than changes in the gas composition of each process step). The QMS sampled the process through a 1/4-inch VCR compression fitting welded to the exhaust elbow of the process pump (Figure 8). The gases of interest are therefore diluted by any pump purge (Section 2.3). The QMS sample inlet pressure was 750 Torr throughout as measured by a capacitance manometer. Sample lines were 1/8-inch stainless steel GC tubing, except the three foot length of 1/4-inch EP 316L tubing connecting the QMS and FTIR instruments. All sample lines were heat traced to ~100°C.

The mass locations were determined using N_2 (7, 14, 28 amu) and NF_3 (71 and 52 amu). The QMS instrument was directly calibrated for NF_3, SiF_4, and F_2 using 1% gas. Five-point or better calibration curves (Appendix A) were measured using dynamic dilution methods to generate concentrations <10,000 ppm.

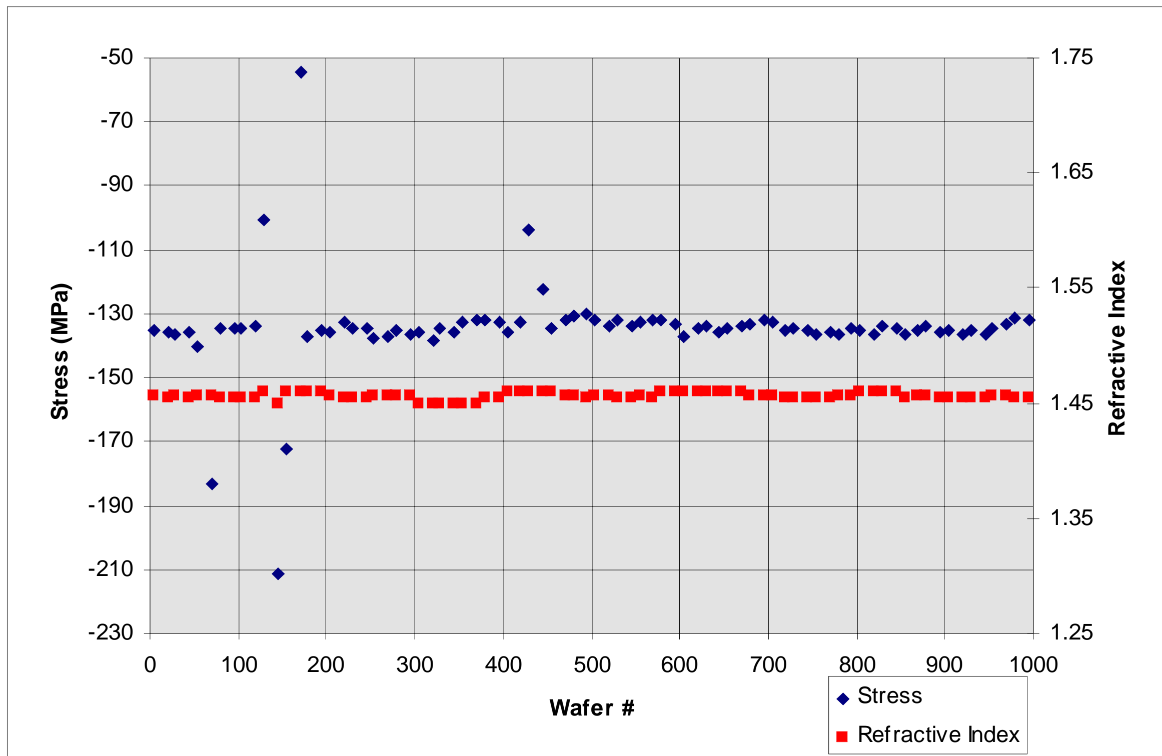


Figure 7 Film Stress and RI Data for the 1000-Wafer Test Run

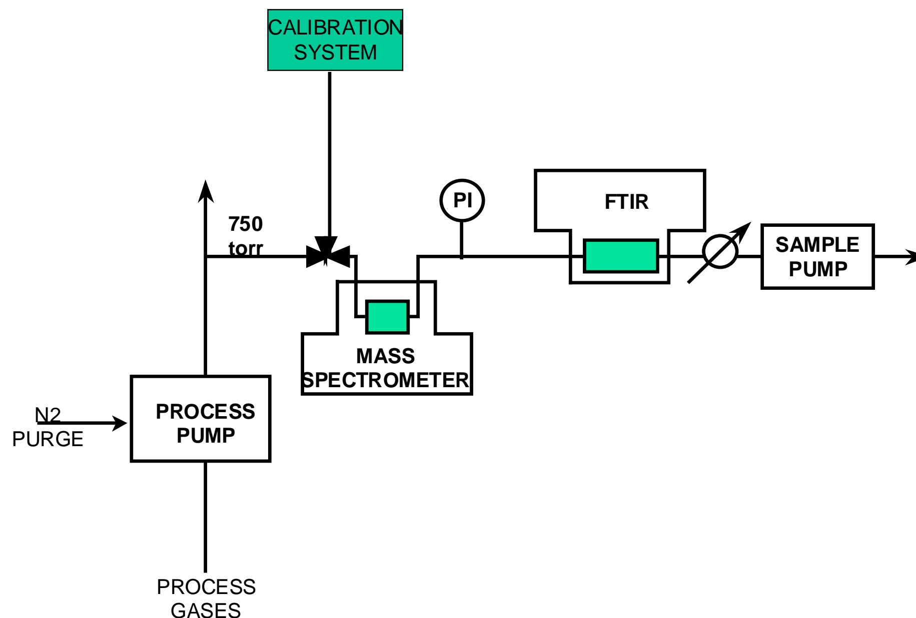


Figure 8 Schematic of the Sampling and Analytical Systems

4.3.1.2 FTIR Measurements of HF

HF concentrations were determined using a Midac I2000 FTIR spectrometer with a HgCdTe detector and a 0.01 m Axiom gas cell. Absorbance from the rotational-vibrational transitions at 4038 cm^{-1} was used as a monitor of the HF concentrations. Absorbance spectra were collected at 1.0 cm^{-1} resolution averaged over eight scans. The FTIR spectrometer was directly calibrated ex situ for HF measurement using a 0.5 % HF gas standard. These concentrations were determined from a single-point calibration; however, the chosen calibration point (54 ppm) was higher than the measured value (~10 ppm).

4.3.1.3 Pump Purge Measurement

Because measurements are made downstream of the process pump (Figure 8), the process byproducts are diluted by the pump purge and make-up air. It is important to know the total gas flow to determine volumetric emissions (i.e., standard cubic centimeters). The pump purge was determined by flowing NF_3 (1500 sccm, 1000 sccm, 500 sccm, and 0 sccm) from the gas panel and measuring its concentration (Figure 9) using the QMS, which has been independently calibrated for NF_3. Figure 10 shows the measured NF_3 concentration as a function of NF_3 gas flow. The dilution factor obtained from the slope of Figure 10 is 47,053 sccm.

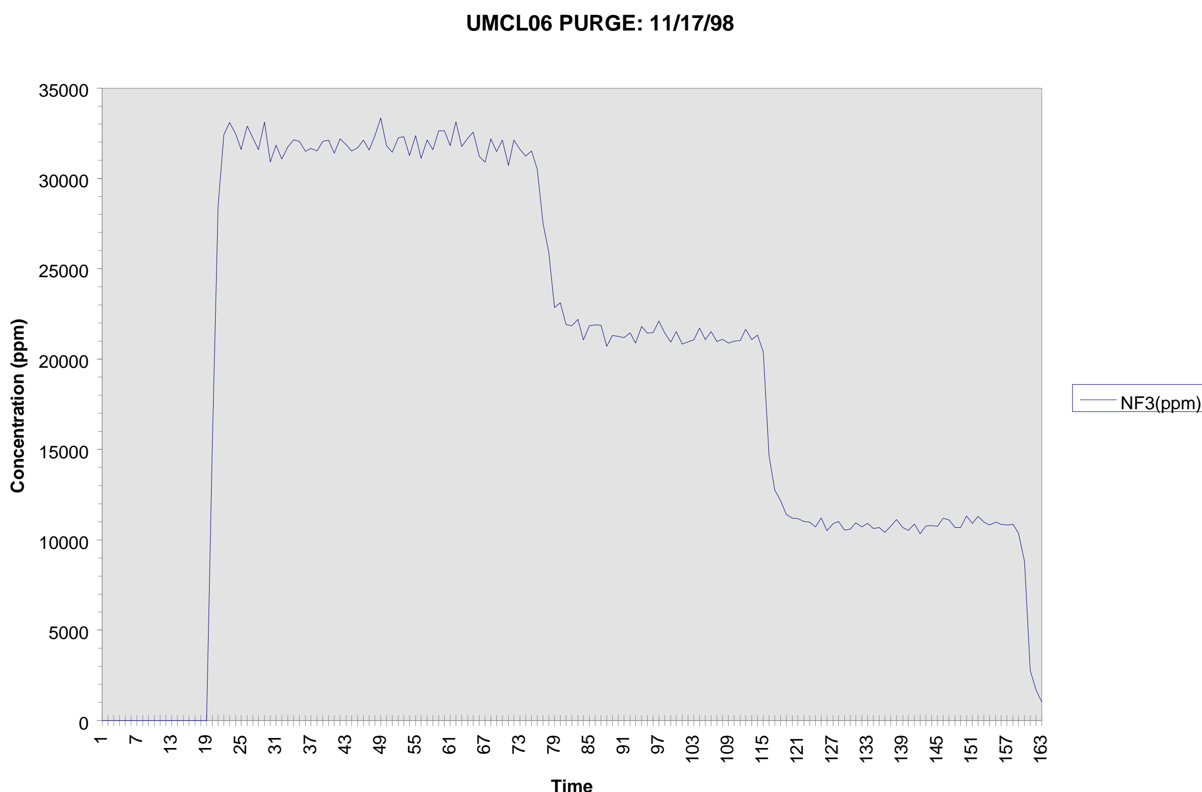


Figure 9 Measurement of NF_3 Concentration Downstream of the Process Pump

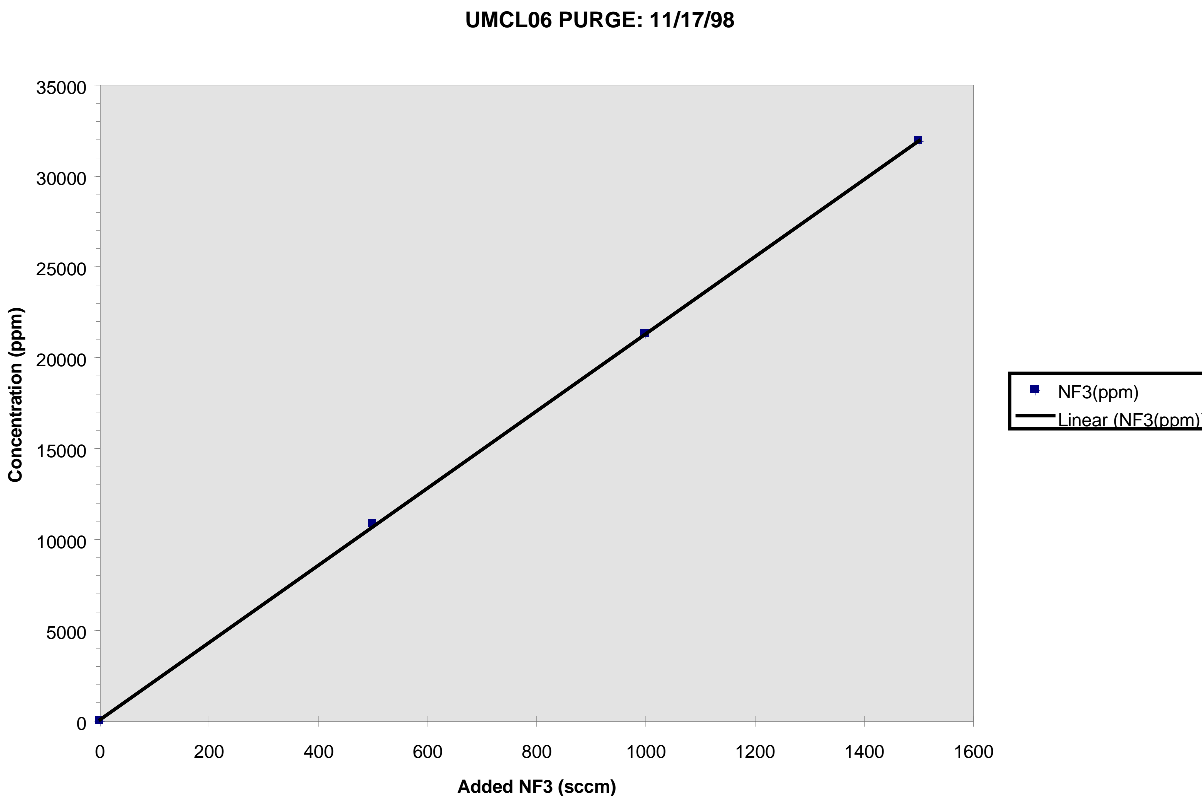


Figure 10 NF_3 Concentration Downstream of Pump vs. NF_3 Gas Flows

4.3.1.4 Error Estimation

The errors contributing to the overall uncertainty of the QMS calibration are summarized in Table 3. Propagation of these errors yields an overall uncertainty in the QMS measurement of 10%.[1]

Table 3 QMS Errors

Source	Error (%)
Gas standards	5
MFC	1 (full scale)
Inlet pressure	1

For the baseline and some DOE processes, the fluorine balance is >100%. More fluorine is detected than can be accounted for from the NF_3 influent since the peak F_2 concentration (~35,000 ppm) is significantly higher than the maximum calibration point (10,000 ppm). The upper calibration limit is determined by the F_2 gas standard available (1%). Concentration measurements outside the limits of the calibration curve result in substantial error. Confirmation that the error is associated with the F_2 measurement is that the fluorine balance is 99% with

[1] "Dynamic Dilution Calibration System for Calibrating Analytical Instruments Used in Gas Analysis," S.N. Ketkar, A. D. Scott, and J. V. Martinez de Pinillos, Air Products and Chemicals, Inc., J. Electrochem. Soc., **141** 184 (1994).

endpoint detection. Also, the fluorine balance is 104% for processes using a 0.5 slm NF_3 flow. Under these conditions, the peak F_2 concentration is only ~15,000 ppm.

4.3.2 Baseline ASTRON Clean Results

The 4250 cm^{-1} absorbance spectrum (Figure 11) and 200 amu mass spectrum (Figure 12) collected during the ASTeX NF_3 clean process identify the byproducts as NF_3, SiF_4, F_2, and HF. The concentration of NF_3, SiF_4, and F_2 during the baseline ASTeX clean process is shown in Figure 13. The HF concentration, measured by FTIR during wafer processing is shown in Figure 14. The HF emissions during the clean result from hydrogen in the TEOS film. The first four processes (PASS1, PASS2, PASS3, PASS4) were run with a clean chamber (i.e., no deposition) to passivate the gas lines with fluorine. Note that the SiF_4 emissions are much lower than with the baseline process (the SiF_4 emissions are not zero, however, since the clean process does include a seasoning step). The emissions associated with these processes were not included in the average emissions reported in Table 4. The NF_3 concentration remains low (<100 ppm) because of a high utilization (greater than 99%). Once the ASTRON power is applied, the SiF_4 concentration sharply increases as the chamber is cleaned. The dominant byproduct of the clean process is F_2 (2855 scc for 120 sec. of operation). Using the point at which the SiF_4 signal drops to 10% of its peak value (350 ppm) as an indicator that the clean is over, endpoint is reached after 60 seconds for the 5000 Å film (0.5 μm). This endpoint time is significantly longer than the time required to actually clean the process chamber (which is approximately 41 sec. for the 5000 Å film) because the free fluorine generated by the ASTRON unit continues to clean residue beyond the wafer area in the chamber and into the foreline. Both the pre-marathon and the marathon results indicated that the actual chamber clean time was significantly less than the time indicated by the endpoint experiments. During the emissions characterization, the clean was run for 120 sec., a significant over-etch, to ensure that endpoint would be detected.

Integrating under the concentration profiles (Figure 13 and Figure 14) allows the volumetric emissions to be calculated. The corresponding NF_3, SiF_4, F_2, and HF emissions for the 120 sec. ASTRON clean process are summarized in Table 4. Process emissions without the over-etch (i.e., to endpoint of 60 sec. for 5000 Å film) are NF_3 (3 scc), SiF_4 (62 scc), F_2 (815 scc), and HF (60 scc). These emissions could be reduced further if the clean was run for only the 41 sec. required to actually clean the process chamber. The first row (NF_3 influent) represents the amount of NF_3 supplied during the clean. This value was obtained by running the baseline clean process with no power applied to the ASTRON source (Figure 15). Integrating under this concentration profile yields the NF_3 influent. Rows 3–6 summarize the NF_3, SiF_4, F_2, and HF emissions, respectively. Using the volumetric emissions of NF_3 and ratioing this to the NF_3 influent value, the NF_3 utilization is calculated to be greater than 99% (row 10). Using the volumetric emissions of the fluorine byproducts and their molecular formulae, the total amount of fluorine emitted can be calculated. Comparing this value to the average fluorine influent (NF_3 influent) gives the fluorine balance (row 8). For the four processed wafers, the fluorine balance is 113%. More fluorine is detected than can be accounted for from the NF_3 influent since the peak F_2 concentration is >35,000 ppm, significantly higher than the maximum calibration point (10,000 ppm).

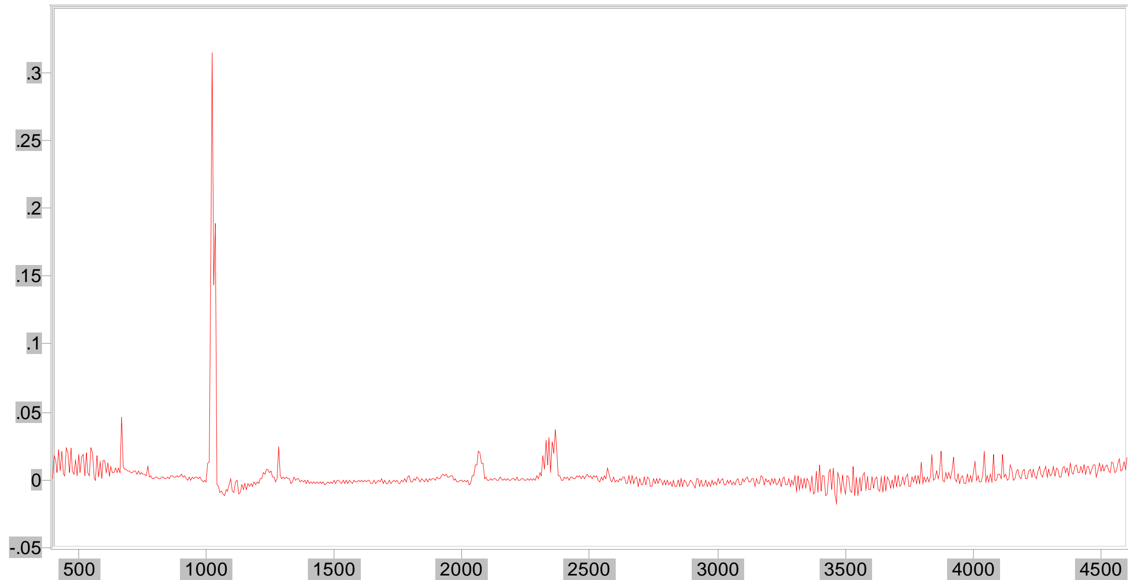


Figure 11 FTIR Absorbance Spectrum for the ASTRON NF_3 Clean Process

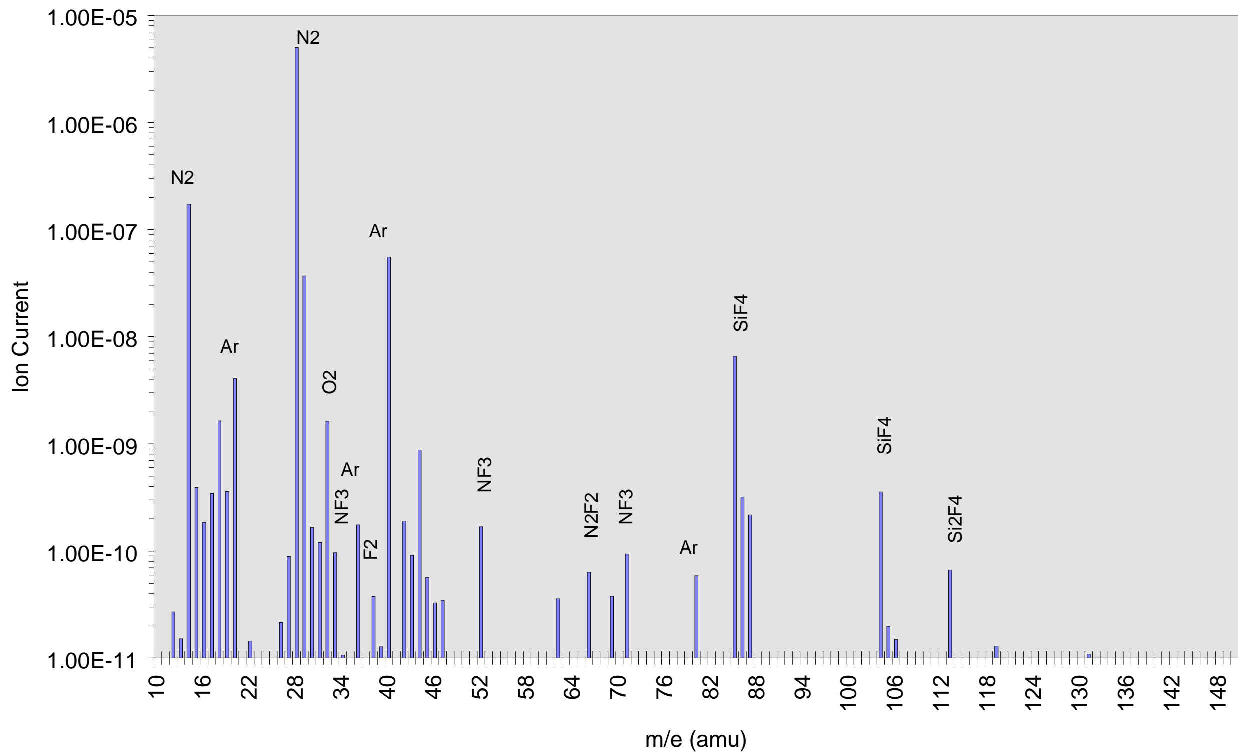


Figure 12 Mass Spectrum for the ASTRON NF_3 Clean Process

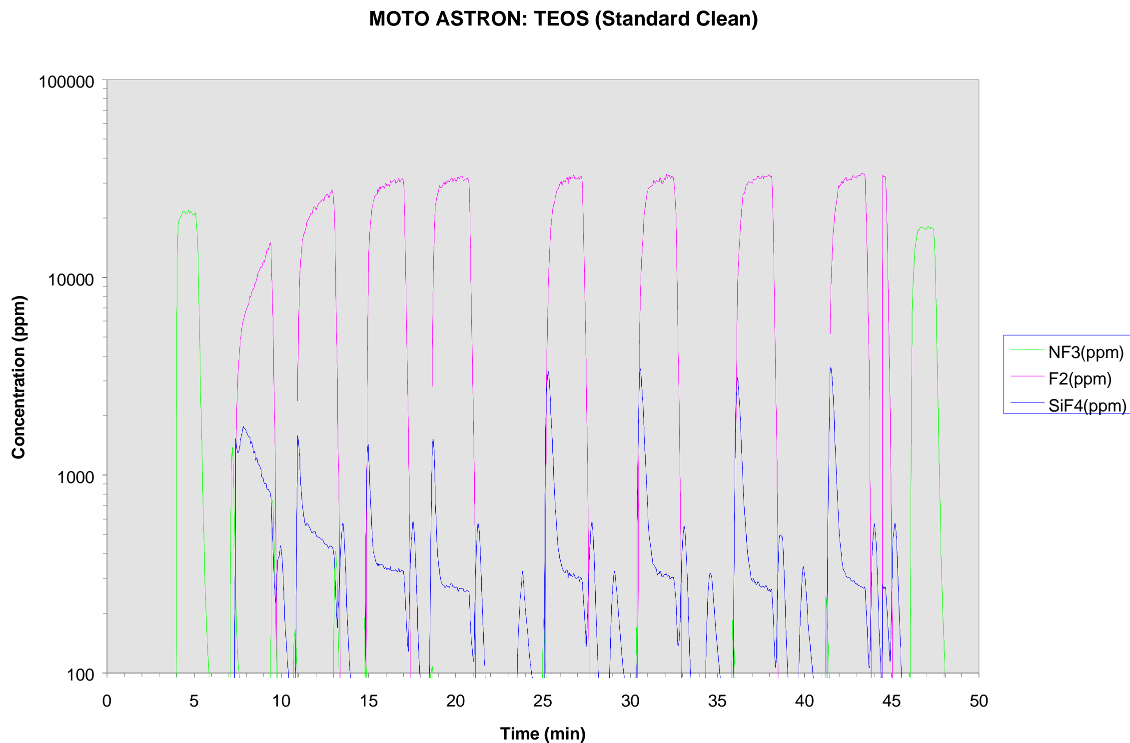


Figure 13 QMS Spectrum During the Baseline ASTRON Clean Process

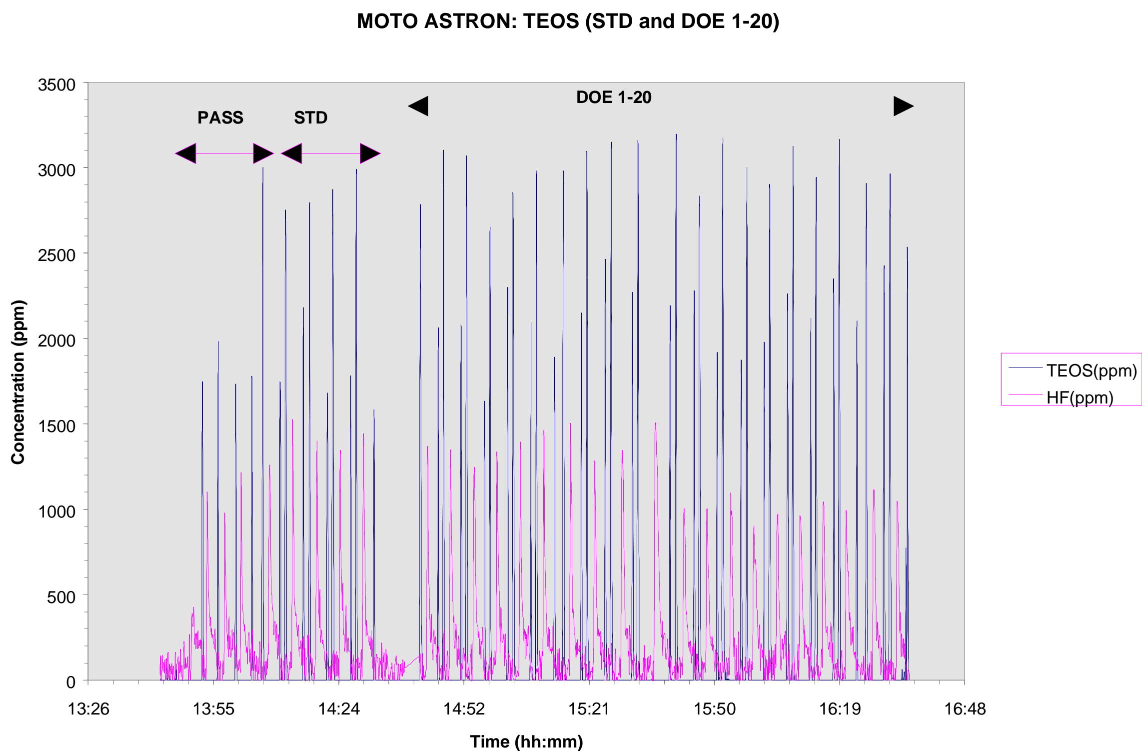


Figure 14 Concentrations of TEOS and HF for Runs 1–20 (by FTIR)

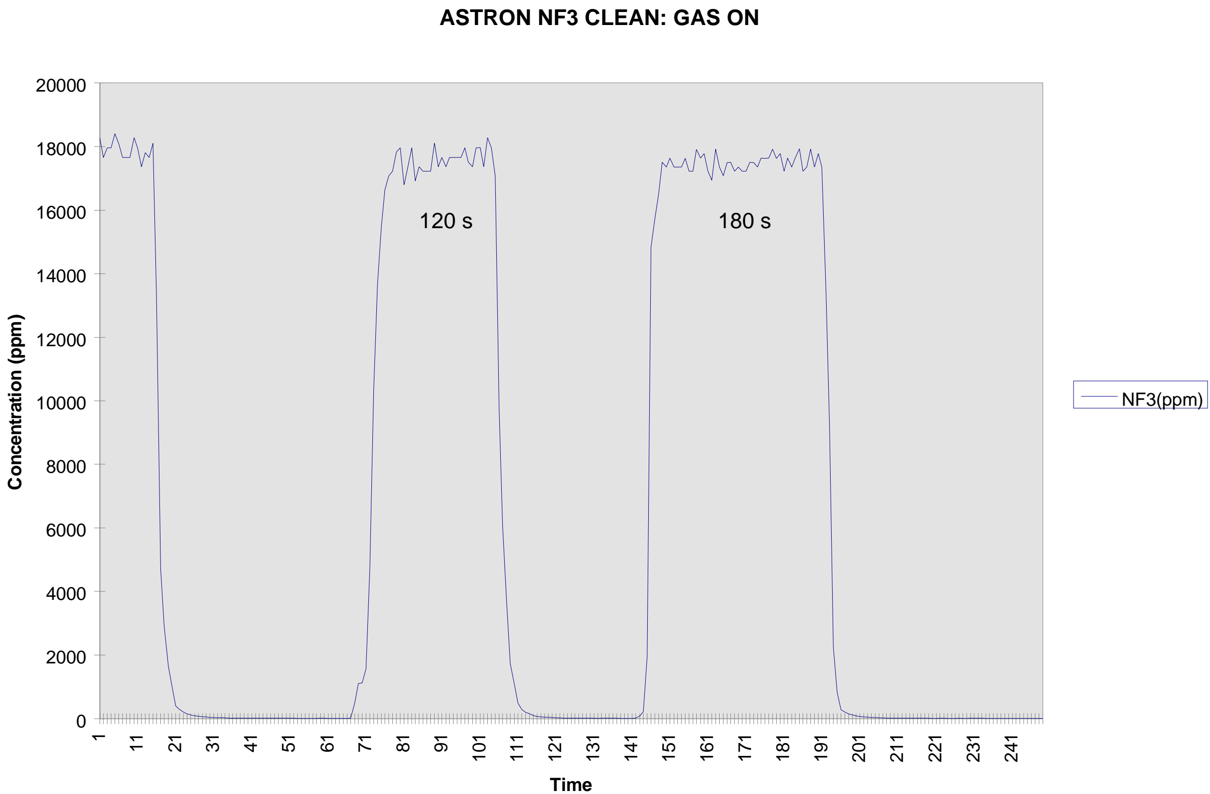


Figure 15 Mass Spectrum for the Baseline Clean Process Without Power to the ASTRON

Table 4 Volumetric Emissions for the TEOS (5000 Å) Chamber Clean at 120 sec.

Row		PASS1	PASS2	PASS3	PASS4	1	2	3	4	Avg.	Endpoint ON
1	NF_3 influent (scc)	1809	1809	1809	1809	1809	1809	1809	1809	**1809**	
2											
3	NF_3 (scc)	31	12	7	7	7	7	7	7	**7**	**3**
4	SiF_4 (scc)	141	76	62	46	89	90	80	83	**86**	**62**
5	F_2 (scc)	924	2171	2935	3038	2845	2804	2894	2878	**2855**	**815**
6	HF (scc)	42	42	43	11	57	60	62	60	**60**	
7											
8	F Balance	0.47	0.87	1.14	1.16	1.13	1.11	1.14	1.14	**1.13**	
9											
10	Utilization (%)	98.3	99.3	99.6	99.6	99.6	99.6	99.6	99.6	**99.6**	

4.3.3 Design of Experiments (DOE) Results

The primary concern of the ASTRON remote plasma clean technology is the amount of NF_3 used. Not only is NF_3 a costly gas, but a significant amount of fluorine is generated as a byproduct of the clean (see Table 4). A process optimization study was conducted to determine the effects of NF_3 gas flow, Ar diluent flow, susceptor spacing, and pressure on the clean endpoint time and NF_3 utilization efficiency. The process emissions, NF_3 utilization, fluorine balance, and endpoint for this series of 37 experiments are summarized in Table 5–Table 7. Throughout the entire process range, the NF_3 utilization was greater than 99%.

For the 37 experiments, the electrode spacing was 180 mils, except for runs #2 and #4, for which the spacing was set to 500 mils.

Table 5 Process Optimization, NF_3 Flow = 1.0 slm (1000 sccm)

	1	2	3	4	5	6	7	8	9	10
NF_3 influent (scc)	1809	1809	1809	1809	1809	1809	1809	1809	1809	2597
NF_3 (scc)	8	7	6	7	6	6	6	7	6	9
SiF_4 (scc)	91	82	72	68	74	91	74	62	126	211
F_2 (scc)	2831	2889	2923	2945	2979	2878	2912	2800	2816	3962
HF (scc)	53	57	61	60	59	55	62	57	71	105
F Balance	1.12	1.14	1.15	1.15	1.17	1.14	1.14	1.09	1.15	1.14
End point (sec.)	55	52	55	60	55	51	51	53	79	109
Utilization (%)	99.5	99.6	99.7	99.6	99.7	99.7	99.7	99.6	99.6	99.7
NF_3 (slm)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ar (slm)	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	1.0	1.0
Pressure (Torr)	2.1/TVO	2.1/TVO	6.0	6.0	4.0	TVO	4.0	6.0	2.1/TVO	2.1/TVO
Film (μm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	2.0

TVO = throttle valve open (lowest pressure)

Table 6 Process Optimization, NF_3 Flow = 0.5 slm (500 sccm)

	11	12	13	14	15	16	17	18	19	20	21	22	23	24
NF_3 influent (scc)	904	904	904	904	904	904	904	904	904	904	904	904	1299	1732
NF_3 (scc)	7	7	6	7	7	7	6	6	6	6	6	6	8	10
SiF_4 (scc)	95	75	63	64	105	91	67	62	111	102	72	56	118	203
F_2 (scc)	1213	1208	1239	1256	1094	1183	1225	1203	1144	1145	1209	1233	1765	2226
HF (scc)	55	53	47	54	51	49	54	53	56	50	50	56	74	108
F Balance	1.06	1.03	1.03	1.05	0.99	1.03	1.03	1.00	1.03	1.02	1.02	1.02	1.05	1.04
End point (sec)	58	63	78	104	55	60	69	89	58	57	68	80	86	132
Utilization (%)	99.2	99.2	99.3	99.3	99.2	99.2	99.3	99.4	99.4	99.3	99.4	99.4	99.4	99.4
NF_3 (slm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ar (slm)	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	0.5	0.5
Pressure (Torr)	TVO	2.1	4.0	6.0	TVO	2.1	4.0	6.0	TVO	2.1	4.0	6.0	2.1	2.1
Film (µm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	2.0

TVO = throttle valve open (lowest pressure)

Table 7 Process Optimization, NF_3 Flow = 0.75 slm (750 sccm)

	25	26	27	28	29	30	31	32	33	34	35	36	37
NF_3 influent (scc)	1357	1357	1357	1357	1357	1357	1357	1357	1357	1357	1357	1948	2598
NF_3 (scc)	7	7	6	6	6	6	6	6	6	7	5	9	10
SiF_4 (scc)	98	67	69	64	86	102	72	68	96	46	72	122	219
F_2 (scc)	2026	2033	2128	2149	2068	2089	2211	2155	2129	2100	2172	3127	4030
HF (scc)	51	49	49	57	54	52	54	53	53	53	52	79	117
F Balance	1.11	1.08	1.13	1.14	1.12	1.14	1.17	1.14	1.16	1.10	1.15	1.17	1.17
End point (sec)	55	58	60	74	53	56	59	66	59	59	62	82	112
Utilization (%)	99.5	99.5	99.5	99.6	99.6	99.6	99.6	99.6	99.6	99.5	99.6	99.6	99.6
NF_3 (slm)	0.75	0.75	0758	0.75	0.75	0.75	0.75	0.75	075	0.75	0.75	0.75	0.75
Ar (slm)	0.75	0.75	0.75	0.75	1.5	1.5	1.5	1.5	2.0	2.0	2.0	0.75	0.75
Pressure (Torr)	TVO	2.1	4.0	6.0	TVO	2.1	4.0	6.0	TVO	4.0	6.0	2.1	2.1
Film (µm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	2.0

TVO = throttle valve open (lowest pressure)

Concentrations of NF_3, SiF_4, and F_2 for the 37-experiment optimization study are shown in Figure 16 and Figure 17. The corresponding HF and TEOS concentrations are shown in Figure 14 and Figure 18. Results from this optimization study (emissions, endpoint time, fluorine balance, and NF_3 utilization) are summarized in Table 5–Table 7. The inflection point in the SiF_4 profile was used as an arbitrary endpoint.

Figure 19 shows the endpoint time as a function of film thickness for NF_3 gas flows of 1.0 slm, 0.75 slm, and 0.5 slm. For all of these processes, the NF_3:Ar ratio was 1.0, the pressure 2.1 Torr, and the electrode spacing 180 mil. The time to clean the process chamber is seen to increase with film thickness.

Figure 19 also indicates that the clean time increases with decreasing NF_3 flow, but only by a few seconds. The NF_3 flow dependence is shown again in Figure 20, where the endpoint time is plotted as a function of NF_3 gas flow. For this set of experiments, the NF_3:Ar ratio was 1.00, the electrode spacing was 180 mil, and the film thickness was 0.5 µm. A comparison of the endpoint times with respect to NF_3 flow for a 1 µm film is shown in Table 8. Note that the endpoint time increased only 7 sec. when the NF_3 flow was reduced by half.

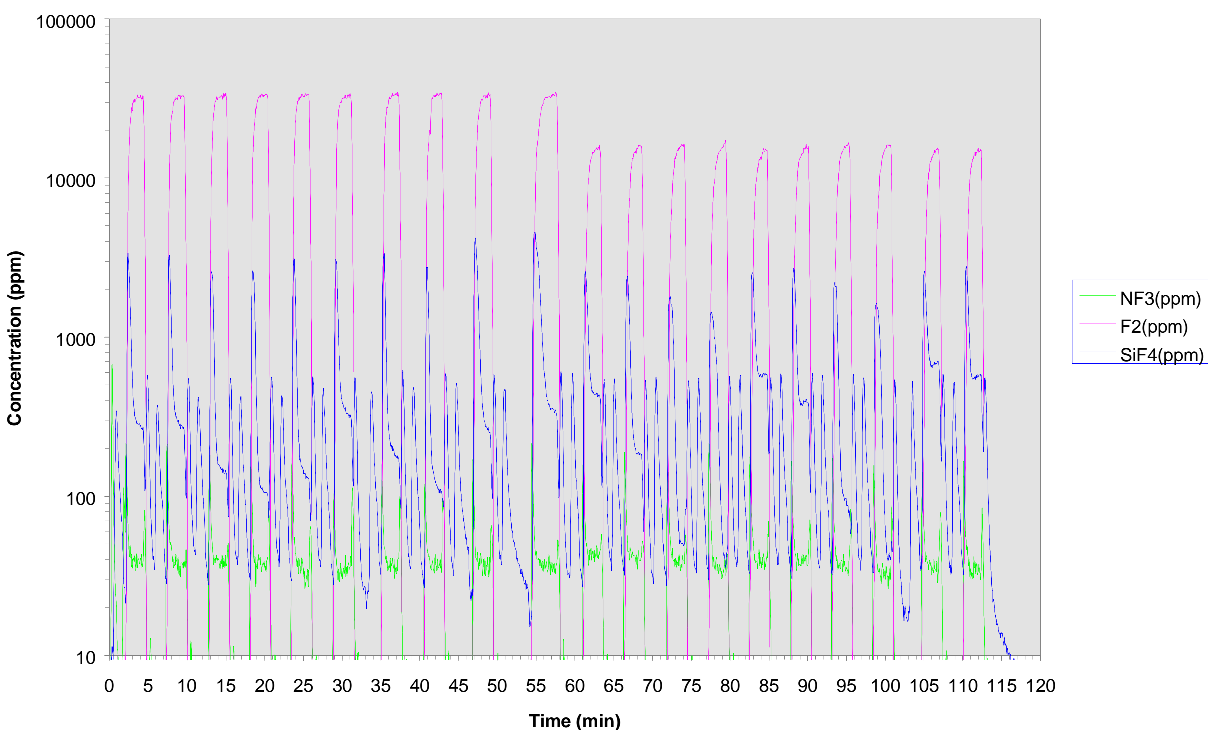


Figure 16 Concentrations of NF_3, SiF_4, and F_2 for Runs 1–20 (by QMS)

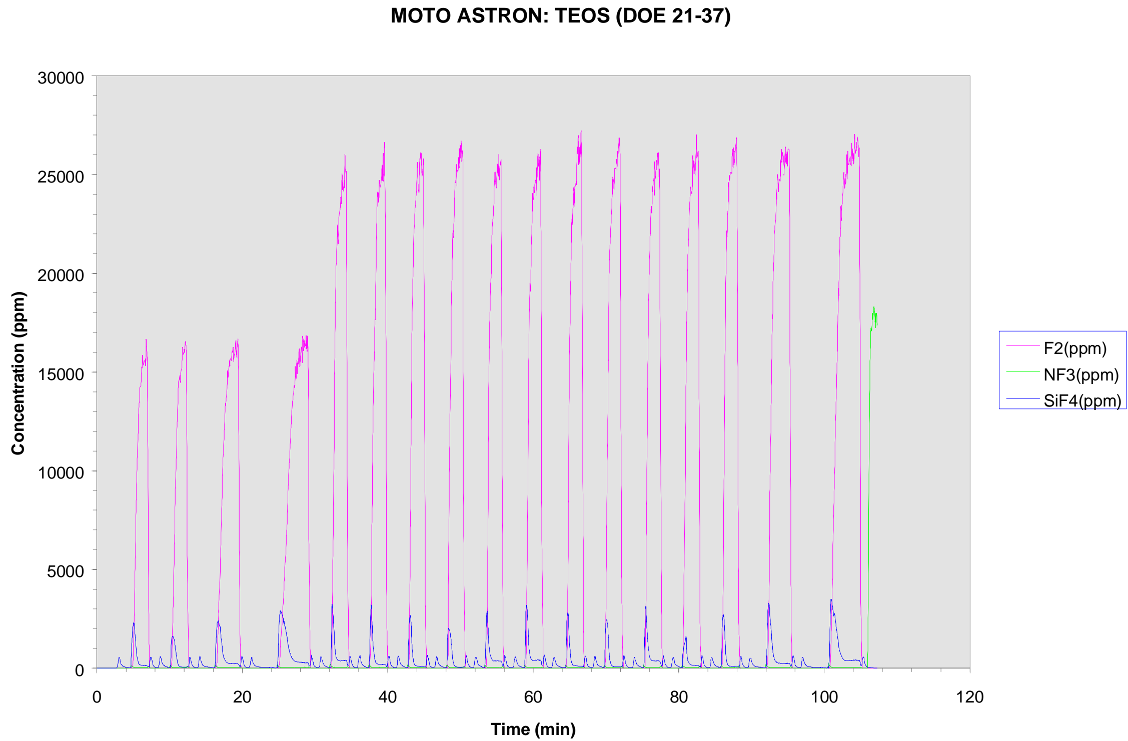


Figure 17 Concentrations of NF_3, SiF_4, and F_2 for Runs 21–37 (by QMS)

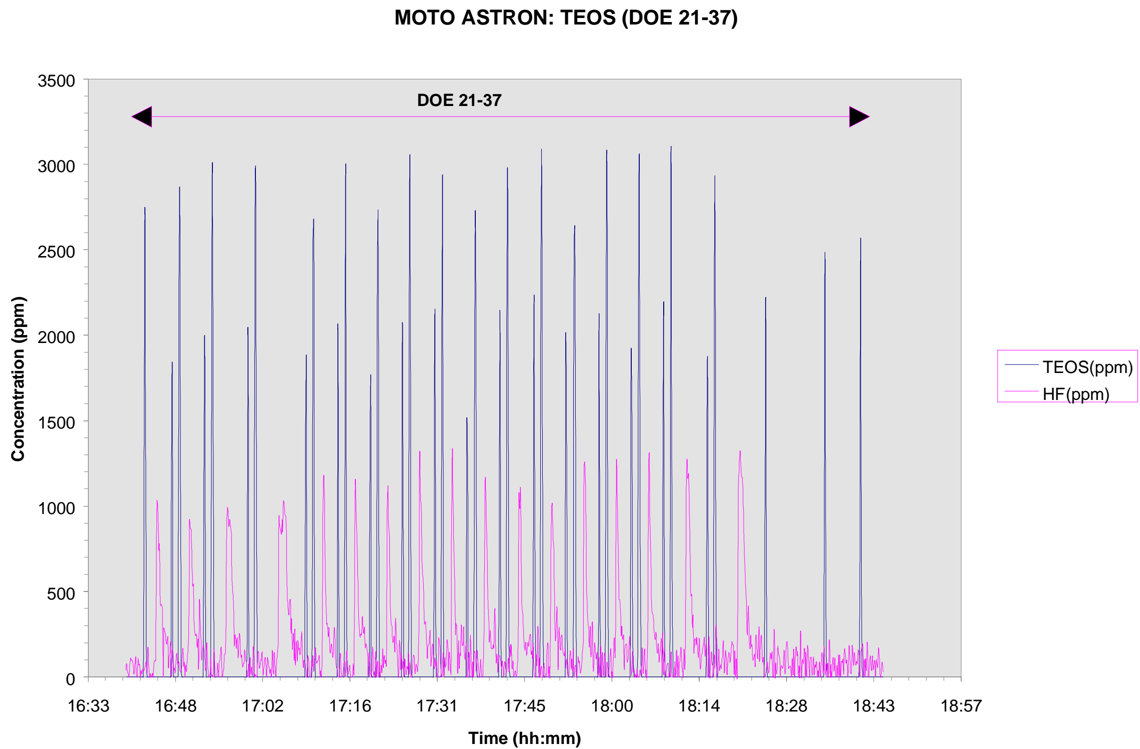


Figure 18 Concentrations of TEOS and HF for Runs 21–37 (by FTIR)

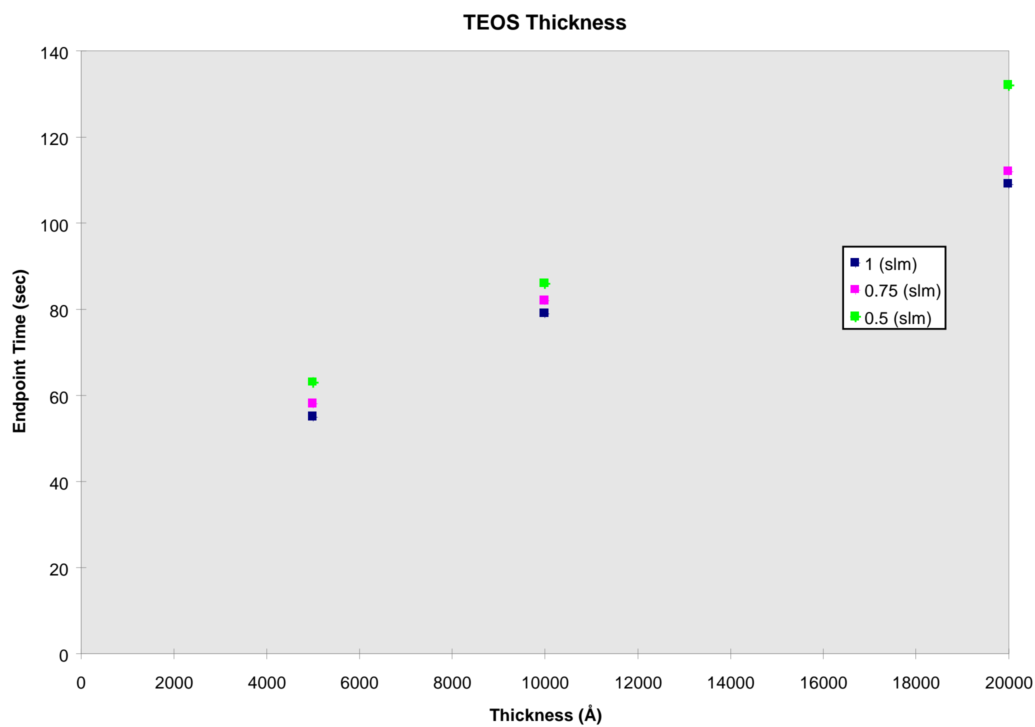


Figure 19 Endpoint Time vs. Film Thickness for Various NF_3 Flows

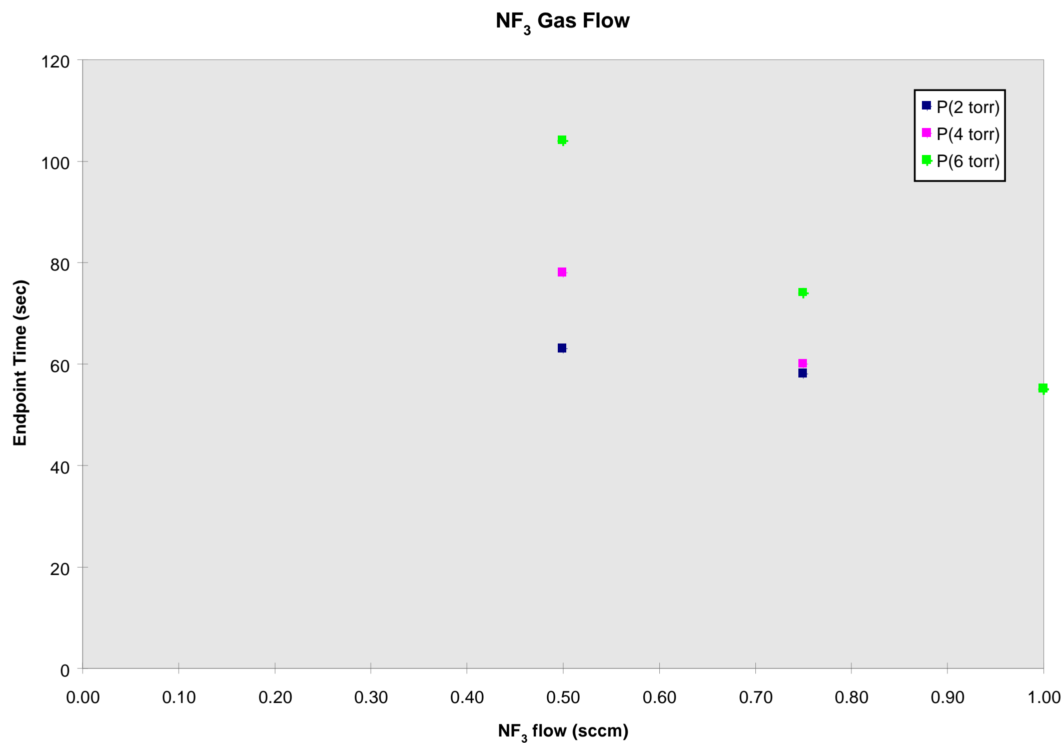


Figure 20 Endpoint Time vs. NF_3 Gas Flow

Table 8 Clean Times for 1 µm Film; Pressure = 2.1 Torr; Ar:NF_3 = 1:1; Electrode Spacing = 180 mils

NF_3 flow (sccm)	Endpoint Time(s)
1000	79
750	82
500	86

The pressure dependence of the endpoint time is also shown in Figure 20. For an NF_3 flow of 1.0 slm, the sensitivity of endpoint time to pressure was not significant. For lower NF_3 flows (0.5 slm and 0.75 slm) however, the clean time increases with increasing pressure. For example, when the NF_3 gas flow is 0.5 slm, the endpoint time increases from 63 sec. to 104 sec. as the pressure is raised from 2 Torr to 6 Torr.

For the film thickness, NF_3 flow, and pressure dependencies discussed so far, the Ar:NF_3 ratio has been fixed at 1.00. The role of the Ar diluent is shown in Figure 21, where the endpoint time is plotted as a function of the Ar:NF_3 ratio. In general, Ar dilution decreases the endpoint time. For example, when the NF_3 gas flow is 0.5 slm, the endpoint time decreases from 63 sec. to 57 sec. as the Ar flow increases from 0.5 slm to 1.5 slm. The exception appears to be an NF_3 flow of 0.75 slm and an Ar flow of 2 slm (Figure 20).

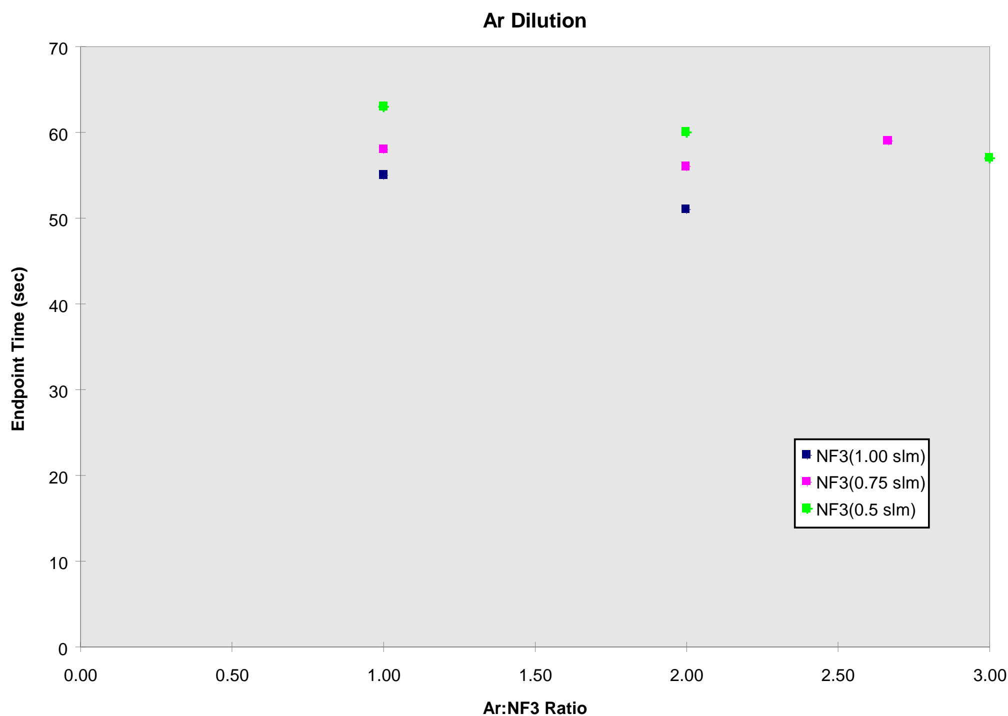


Figure 21 Endpoint Time vs. Ar:NF_3 Ratio

4.4 Post-Evaluation Chamber Inspection Results

After the marathon and DOE were completed, the ASTRON was removed from the chamber lid and the chamber opened for inspection. The chamber body was clean, bare aluminum with no observed defects. The chamber actually looked cleaner than pre-ASTRON installation. This could be attributed to areas of the chamber body being cleaned more effectively because of the high F concentration throughout the chamber during the clean process. The susceptor, sapphire-coated lamp window, view port window, showerhead, and blocker plate were all in new condition. The modified gas-mixing block and sapphire tubes in the constant voltage gradient feedthrough were also in new condition. All of the chamber O-rings were in good condition and held up well to the fluorine process. The actual age of the O-rings is not known; only the O-rings in the gas-mixing block and constant voltage gradient feedthrough were replaced when the ASTRON was installed. The combined total of both the clean optimization and marathon totaled more than 3500 wafers with the modified hardware.

5 SUMMARY/CONCLUSIONS

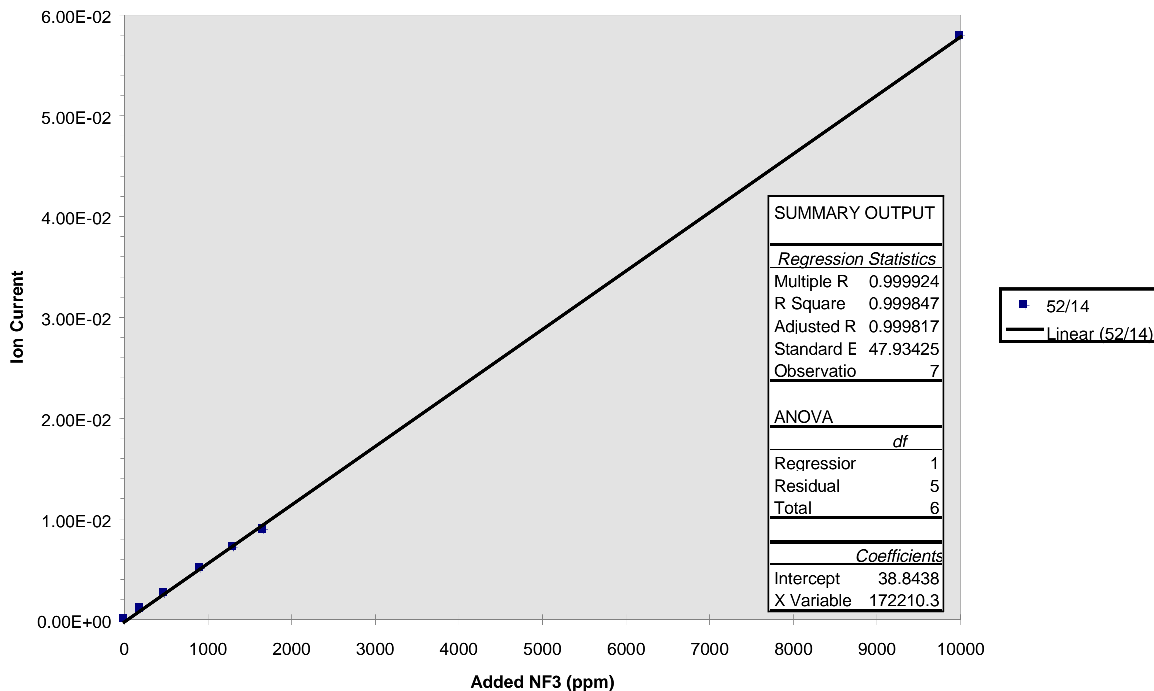
The ASTeX ASTRON atomic fluorine generator has been shown to be effective for 200 mm Applied Materials DxL (lamp heated) TEOS chamber cleaning. Throughout the 1000-wafer marathon, no negative effects on film properties were noted. There was no evidence of particle generation. Process chamber clean times were 30–50% faster than the baseline C_2F_6 clean for PETEOS films.

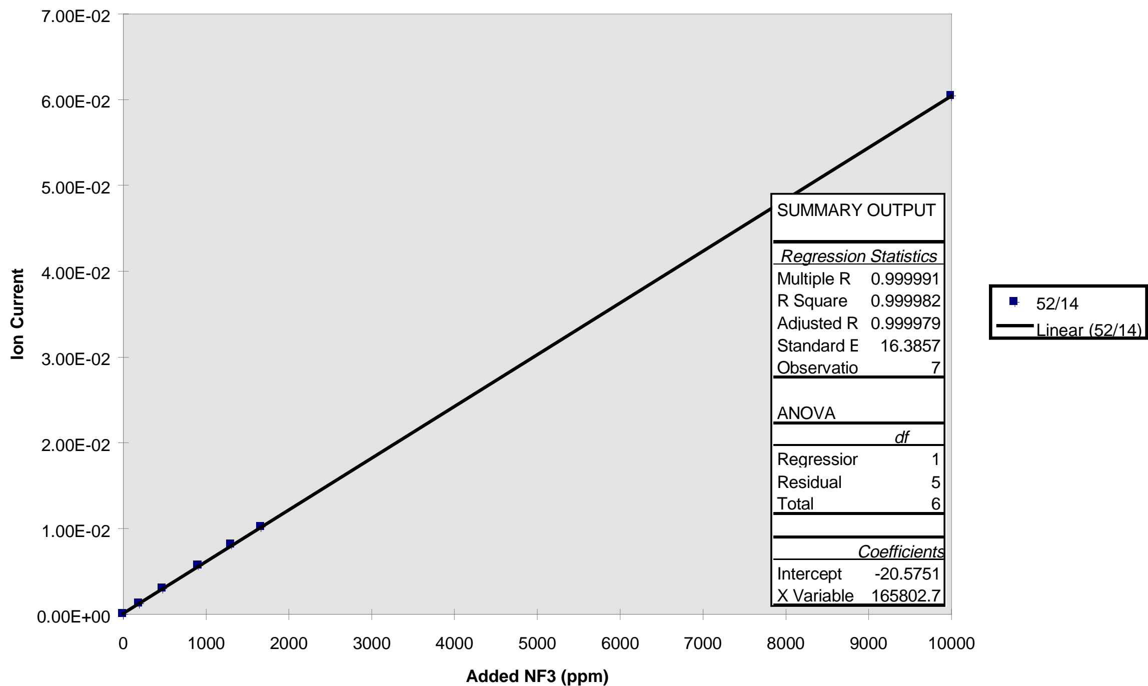
The NF_3 utilization of the ASTRON was demonstrated to be greater than 99% at all process conditions, thus effectively eliminating PFC emissions from the chamber cleaning process. The volumetric emissions (NF_3, SiF_4, F_2, and HF) have been quantified and a fluorine balance of 100% or greater achieved. For a 0.5 µm film, the total amount of F_2 emitted when the clean was operated to endpoint (60 sec.) with 1000 sccm of NF_3 flow was 815 scc. This amount would be significantly reduced if the NF_3 flow was reduced and/or if the clean process was run for only the amount of time necessary to clean the process chamber (41 sec. for 0.5 µm film with 1000 sccm of NF_3 flow).

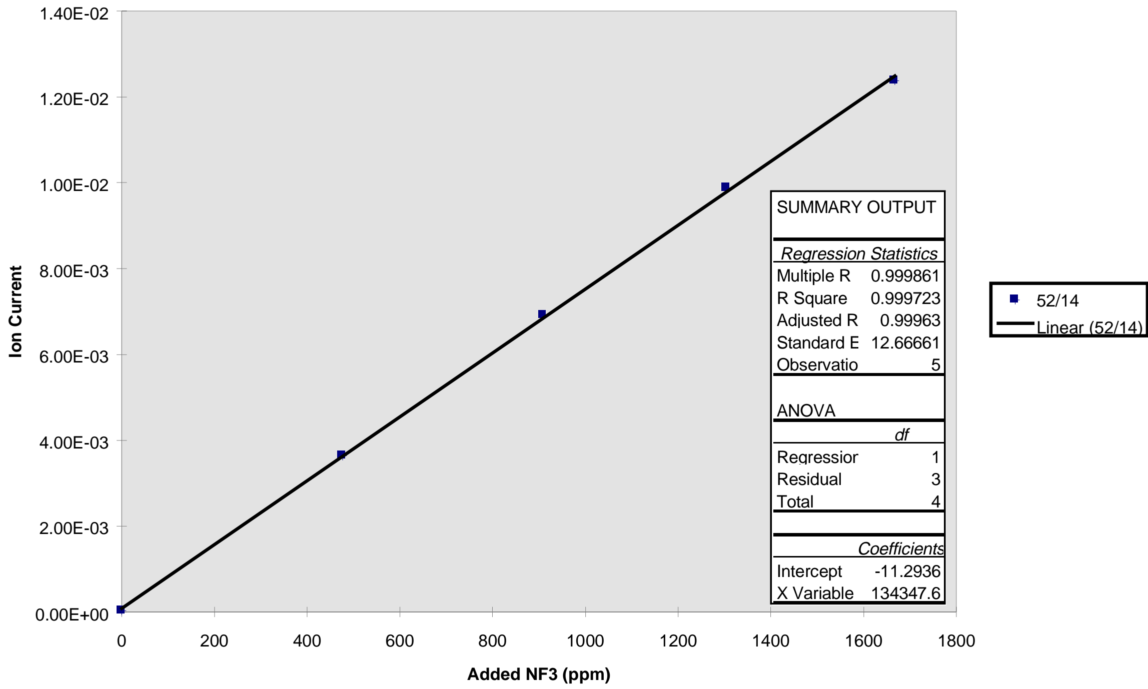
The results of the DOE indicate that the NF_3 flow can be reduced by half—from 1000 sccm to 500 sccm—with no significant increase in endpoint time; the time to endpoint increased by only 7 sec. (9%) for a 1 µm film with this flow decrease (pressure = 2.1 Torr, Ar:NF_3 = 1:1). Endpoint times are shorter at lower chamber pressure. The endpoint time can also be reduced by increasing the Ar:NF_3 ratio. Although further characterization work should be done, the optimum process conditions with respect to clean time, gas flows, and total emissions would likely be an NF_3 flow of 500 sccm (resulting in reduced F_2 emissions and input gas cost without significant impact on clean time) with a pressure of 2.1 Torr (or throttle valve open) and an Ar:NF_3 ratio >1 (to reduce clean time).

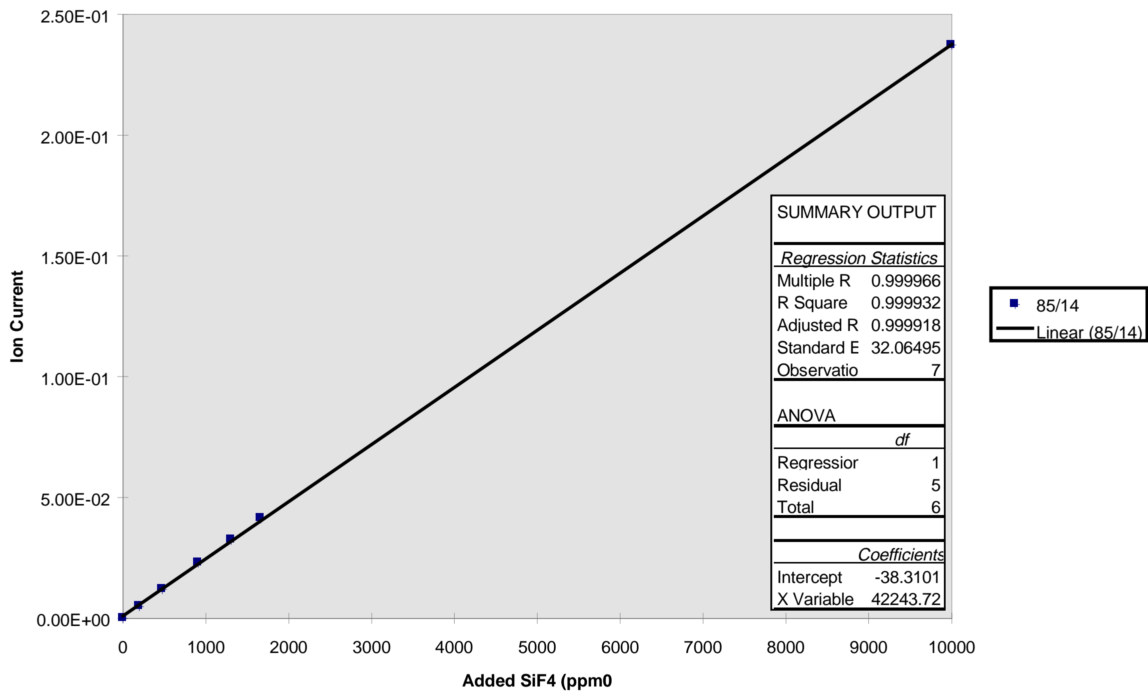
A post-marathon and DOE inspection of the chamber yielded no observable damage to the internal components. The chamber body was clean, bare aluminum with no observed defects. The chamber actually looked cleaner than pre-ASTRON installation. The combined total of both the clean optimization and marathon was more than 3500 wafers with the modified hardware.

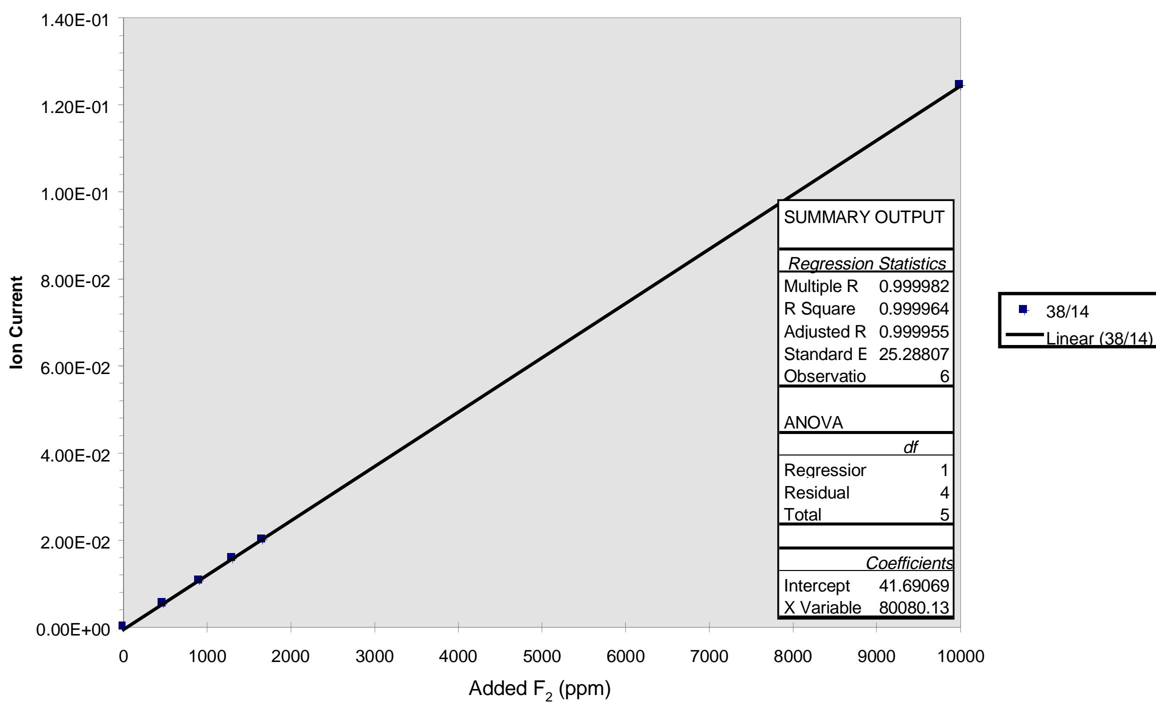
APPENDIX A
QMS Calibration Charts






NF3 CALIBRATION: 11/19b/98
Ion Current
1.40E-02
1.20E-02
1.00E-02
8.00E-03
6.00E-03
4.00E-03
2.00E-03
0.00E+00
0
200
400
600
800
1000
1200
1400
1600
1800
Added NF3 (ppm)
SUMMARY OUTPUT
Regression Statistics
Multiple R 0.999861
R Square 0.999723
Adjusted R 0.99963
Standard E 12.66661
Observatio 5
ANOVA
df
Regressior 1
Residual 3
Total 4
Coefficients
Intercept -11.2936
X Variable 134347.6
52/14
Linear (52/14)


SiF4 CALIBRATION: 11/19/98
Ion Current
2.50E-01
2.00E-01
1.50E-01
1.00E-01
5.00E-02
0.00E+00
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
Added SiF4 (ppm0
SUMMARY OUTPUT
Regression Statistics
Multiple R 0.999966
R Square 0.999932
Adjusted R 0.999918
Standard E 32.06495
Observatio 7
ANOVA
df
Regressior 1
Residual 5
Total 6
Coefficients
Intercept -38.3101
X Variable 42243.72
85/14
Linear (85/14)


F2 CALIBRATION: 11/19/98
1.40E-01
1.20E-01
1.00E-01
8.00E-02
6.00E-02
4.00E-02
2.00E-02
0.00E+00
Ion Current
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
Added F2 (ppm)
SUMMARY OUTPUT
Regression Statistics
Multiple R 0.999982
R Square 0.999964
Adjusted R 0.999955
Standard E 25.28807
Observatio 6
ANOVA
df
Regressior 1
Residual 4
Total 5
Coefficients
Intercept 41.69069
X Variable 80080.13
38/14
Linear (38/14)

SEMATECH Technology Transfer
2706 Montopolis Drive
Austin, TX 78741

http://www.sematech.org
e-mail: info@sematech.org