MINIMIZING PFC AND HAP EMISSIONS DURING ULTIMA HDP-CVD PROCESSING: PSG, USG, AND FSG FILMS

Andrew D. Johnson and Richard V. Pearce
Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA 18195

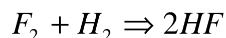
Mat Waltrip, Thanh N. Pham, Patricia M. Jennings, and Jack Branning
Applied Materials, Inc., 3050 Bowers Ave., Santa Clara, CA 95054

In support of a voluntary commitment to minimize process emissions, considerable effort has been expended by semiconductor manufacturers, OEMs, and materials suppliers to identify, quantify, and reduce emissions for individual process steps. This paper describes an emissions reduction program for three Ultima HDP-CVD processes: PSG, USG, and FSG deposition and chamber clean. Quantitative QMS and FTIR measurements show that during thin film deposition the SiH_4 is fully utilized, while for FSG films, the SiF_4 emissions associated with the deposition step is 7 mg/µm. The NF_3 remote microwave process was shown to effectively eliminate PFC emissions from Ultima HDP-CVD cleaning (3 mg/µm). For all three processes, the NF_3 utilization is better than 99 %. The MMTCE for this process is 0.15×10^{-9}, which represents a reduction of more than 90 %. Byproducts of the remote NF_3 clean process were identified as unreacted NF_3, SiF_4, F_2, and HF: 92-100 % of the influent fluorine is accounted for. A Delatech CDO was found to be an effective solution for abating the fluorine effluent from Ultima HDP-CVD processes. Indeed, the Delatech CDO removes 99.8 % of the influent fluorine during Ultima HDP-CVD processing.

INTRODUCTION

Semiconductor manufacturers are concerned about atmospheric emissions associated with wafer fabrication. In support of a voluntary commitment to minimize process emissions, considerable effort has been expended by semiconductor manufacturers, OEMs, and materials suppliers to identify, quantify, and reduce emissions for individual process steps. Initially, industry concern focused upon perfluorocompound (PFC) emissions because they are suspected of contributing to anthropogenic climate change. PFCs in the atmosphere are believed to originate exclusively from anthropogenic uses and, because of their long lifetimes and strong infrared absorbances, could contribute to global warming. The predominant use of PFCs in semiconductor manufacturing is to clean process chambers following thin film CVD. As part of the semiconductor industry's voluntary commitment to minimize PFC emissions, Applied Materials developed a new process for cleaning CVD tools: NF_3 remote microwave clean. This paper describes the characterization of PFC and HAP emissions during Ultima HDP-CVD thin film deposition and chamber cleaning.

Process emissions were identified and quantified by quadrupole mass spectrometry (QMS) and fourier transform infrared spectroscopy (FTIR) measurements (Section 2). Three Ultima HDP-CVD processes were characterized (Section 3): phosphosilicate glass (PSG), undoped silicate glass (USG), and fluorine doped silicate glass (FSG). Besides NF_3, the other gaseous emissions are HF, F_2, and SiF_4. Although NF_3 emissions were dramatically reduced, this characterization determined that F_2 emissions during the clean process were substantial. While F_2 has no global warming potential, it is hazardous material that should not be released to the atmosphere. In section 4, F_2 emissions using a Delatech CDO are described. The Delatech CDO uses a two stage process. The F_2 byproducts are first reduced with H_2 in a combustion chamber:



$$F_2 + H_2 \Rightarrow 2HF$$

The HF byproduct is then scrubbed as HF(aq) using a neutral water scrubber and the waste water that is generated subsequently treated for disposal.

2. EXPERIMENTAL METHODOLOGY

PSG (8,000 A), USG (15,000 A), and FSG (25,000 A) films were deposited in a 200 mm Applied Materials' Ultima HDP-CVD chamber. The deposition gases are SiH_4, PH_3, and SiF_4. O_2 and Ar were the other process gases. After processing 5 PSG wafers, a periodic remote microwave NF_3 process was used to clean the chamber. For the USG and FSG depositions, the process chamber was cleaned after each process.

Process byproducts were measured by QMS and FTIR downstream of the process pump and abatement system. The process was sampled through a 1/4 inch VCR compression fitting welded to the exhaust elbow of the process pump. The gases of interest are therefore diluted by any pump purge (section 2.3). The 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 3 ft. length of ¼ inch EP 316L tubing connecting the QMS and FTIR instruments. All sample lines were heat traced to ~100°C. Before monitoring the Ultima HDP-CVD process, all sample lines were fluorine passivated by running the remote NF_3 clean process in a clean chamber.

2.1 QMS Measurements of NF_3, SiF_4, and F_2

The processes were monitored with a UTI Qualitrace QMS having a 200 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 NF_3 (71 and 52 amu). The QMS instrument was directly calibrated for NF_3, SiF_4, and F_2 using 1 % gas standards. Five (5) point or better calibration curves were measured using dynamic dilution methods to generate concentrations <10,000 ppm. Due to sensitivity changes, the QMS analyzer was calibrated each day.

2.2 FTIR Measurements of SiH_4, PH_3, and HF

SiH_4, PH_3, and HF concentrations were determined using a Midac I2000 FTIR spectrometer with a HgCdTe detector and a Axiom gas cell (0.1 m or 0.01 m). Absorbance spectra were collected at 1.0 cm^{-1} resolution (8 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 (540 ppm.m or 55 ppm.m reference spectra). Absorbance from the rotational-vibrational transition at 4038 cm^{-1} was used as a monitor of the HF concentration. The SiH_4 calibration was obtained using the tool gas panel by diluting the SiH_4 flow (10 -75 sccm) with the pump purge (section 2.3). The Si-H stretch region (2174-2199 cm^{-1}) was used for SiH_4 measurements. A single point calibration was used for SiH_4 determinations (34.4 ppm.m) since the calibration is linear over the concentration range. A library spectrum was used for PH_3 concentration measurements (100 ppm.m) where the region 2302-2381 cm^{-1} was used for concentration measurements.

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 NF_3 from the gas panel and measuring its concentration using the QMS which has been independently calibrated for NF_3 (section 2.1). The dilution factor is obtained from the slope of NF_3 concentration versus NF_3 gas flow. For measurements downstream of the abatement system, NF_3 cannot be used to determine the total gas flow since it thermally decomposes above 500 °C. The total pump purge and makeup air flowing through the Delatech CDO was estimated by flowing He (60 sccm) using the gas panel on the process tool. The He concentration (340 ppm) downstream of the Delatech CDO was measured using the mass spectrometer which had been independently calibrated for He measurements. The total purge causing this dilution is calculated to be 177 slm.

3. ULTIMA HDP-CVD PROCESSING

3.1 PSG Deposition

The 4250 cm^{-1} absorbance spectrum during PSG film deposition is shown in Fig. 1. No SiH_4 or PH_3 features are observed in the region 2000 cm^{-1} to 2500 cm^{-1}. The peaks at 835 cm^{-1} and 1235 cm^{-1} are due to PSG film deposition on the windows of the FTIR gas cell (i.e. they are observed throughout the effluent characterization). Figure 2 shows the concentration of SiH_4 and PH_3 (FTIR measurement) during Ultima HDP-CVD PSG processing. These time profiles confirm that the SiH_4 and PH_3 are completely utilized by this process (SiH_4 and PH_3 are below the FTIR detection limits).

The 4250 cm^{-1} absorbance spectrum (Fig. 3) and 200 amu mass spectrum (Fig. 4) collected during the NF_3 clean process identify the by-products as NF_3, SiF_4, PF_5, F_2, and HF. We conclude that the phosphorous is removed as PF_5 from its QMS cracking pattern: 107 amu (PF_4), 88 amu (PF_3), 69 amu (PF_2), and 50 amu (PF). The concentrations of NF_3, SiF_4, and F_2 during Ultima HDP-CVD PSG processing are shown in Figs. 5. The HF concentration, due to hydrogen in the PSG film, measured by FTIR during wafer processing is shown in Fig. 6. The first two processes (PASS 1 and PASS 2) were run with a clean chamber (i.e. no dep.) for the purpose of fluorine passivating the gas lines (Section 2). The NF_3 concentration remains low (<1000 ppm) due to a high utilization (99 %). Once the MW power is applied, there is a sharp increase in the SiF_4 concentration as the chamber is cleaned. The dominant byproduct of the clean process is elemental F_2.

PSG CLEAN							**AVE**	
	PASS1	**PASS2**	**1**	**2**	**3**	**4**	**(scc)**	**(g/um)**
NF3(scc)	60	41	44	39	38	37	**39**	**0.03**
SiF4(scc)	73	60	687	672	662	651	**668**	**0.78**
PF5	4	3	34	34	33	33	**34**	**0.5**
F2(scc)	8153	9668	7707	8670	8908	8940	**8556**	**3.63**
HF(scc)	122	189	547	539	520	510	**529**	**0.12**
Utilization (%)	99	99	99	99	99	99	**99**	
F-Balance	0.79	0.93	0.89	0.98	0.99	1.00	**0.96**	
PSG DEPOSITION							**AVE**	
	PASS1	**PASS2**	**1**	**2**	**3**	**4**	**(scc)**	**(g/um)**
SiH4(scc)	0	0	0	0	0	0	**0**	**0**
PH3(scc)	0	0	0	0	0	0	**0**	**0**

Table I.

Integrating under the concentration profiles (Figs. 5 and 6) allows the volumetric emissions to be calculated. The corresponding SiH_4, PH_3, NF_3, SiF_4, PF_5, F_2, and HF emissions for the Ultima HDP-CVD PSG process are summarized in Table I. Note that the volumetric emission (scc) represents the cumulative emission for the 5 wafer periodic clean, whereas, the mass emission (g/μm) has been normalized for the film thickness (8,000 A) and number of wafers processed per clean (5). Rows 3-7 summarize the NF_3, SiF_4, PF_5, F_2, and HF emissions, respectively. Using the volumetric emissions of NF_3, and ratioing this to the NF_3 influent, the NF_3 utilization is calculated to be 99 % (row 9). 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 fluorine influent gives the fluorine balance. The fluorine influent was obtained by multiplying the NF_3 flow rate by the clean time. For the 25 processed wafers, the fluorine balance is 96 % indicating that all of the fluorine byproducts have been accounted for.

3.2 USG Deposition

Concentrations of SiH_4, HF, NF_3, SiF_4, and F_2 are shown in Figs. 7 and 8. As for PSG deposition, the SiH_4 is completely utilized during USG HDP-CVD (Fig. 7). Volumetric emissions during Ultima HDP-CVD USG processing are summarized in Table II. The NF_3 utilization for this clean process is 100 % with 92 % of the fluorine being accounted for.

	1	2	3	AVE
NF3 (scc)	30	18	18	**22**
SiF4 (scc)	270	221	255	**249**
F2 (scc)	6939	7054	7175	**7056**
HF (scc)	18	18	18	**18**
F Balance	*0.91*	*0.91*	*0.94*	**0.92**
Utilization(%)	0.99	1.00	1.00	**1.00**

Table II.

3.3 FSG Deposition

Concentrations of SiH_4, HF, NF_3, SiF_4, and F_2 during the deposition and clean process are shown in Figs. 9 and 10. The SiH_4 is completely utilized during FSG HDP-CVD (Fig. 9). Note that these FTIR measurements cannot be used to establish SiF_4 emissions during the clean due to the high concentration (Fig. 10) saturating the infrared region. FTIR data are, however, used to determine the SiF_4 emissions during the deposition. Volumetric emissions during Ultima HDP-CVD FSG are summarized in Table III and IV for the deposition and clean processes, respectively. The NF_3 utilization for this clean process is 99.7 %, and 100 % of the fluorine is accounted for. The NF_3 influent value was obtained by running the clean process with no microwave power applied. This method accounts for any variation in the MFC calibration.

DEP (scc)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
SiF_4	37	29	35	39	29		30	28	38	55	34	34	53
HF	62	54	53	57	50		53	50	54	56	47	49	58
SiH_4	4	0	0	3	0		0	0	0	0	0	0	1

Table III

	1	2	3	AVE
NF3 (scc)	40	27	29	**32**

SiF4 (scc)	793	849	817	**820**
F2 (scc)	13559	13443	13562	**13522**
HF (scc)	99	99	99	**99**
F Balance	*1.00*	*1.00*	*1.00*	**1.00**
Utilization (%)	99.6	99.7	99.7	**99.7**

Table IV

4. ULTIMA HDP-CVD PROCESS ABATEMENT

The NF_3 remote plasma source has been shown (Section 3) to essentially eliminate PFC emissions from Ultima HDP-CVD processes. The dominant byproduct during the clean is now elemental F_2. Abatement of both USG (15 kA) and FSG (25 kA) processes by a Delatech CDO was characterized. For each process, three wafers were processed. The concentrations of NF_3 , SiF_4, and F_2 during CVD and the subsequent clean are shown in Fig. 11. At the start of the clean process, the NF_3 concentration spikes to ~90 ppm. During the clean and overetch, however, the NF_3 is at baseline levels. The SiF_4 concentration increases to 5 ppm during the main etch then returns to baseline levels once the chamber is clean. The NF_3 utilization is >99 %, in agreement with the earlier studies. The dominant byproduct of the remote NF_3 clean process downstream from the reactor is F_2, whose concentration is ~20 ppm throughout the clean process. The volumetric NF_3, SiF_4, and F_2 emissions downstream of the Delatech CDO are summarized in tables V for the USG and FSG processes. These emissions are based upon a purge flow of 177 slm (section 2.3). Also shown in table V are the process emissions before the Delatech CDO. Elemental F_2 emissions for both the USG and FSG process are reduced by 99.8 % downstream of the Delatech CDO.

	USG (15 kA)		**FSG (25 kA)**	
	BEFORE CDO	*AFTER CDO*	*BEFORE CDO*	*AFTER CDO*
NF_3 (scc)	22	7	32	10
SiF_4 (scc)	249	1	820	2
F_2 (scc)	7,056	13	13,522	31
HF (scc)	100	n/a	100	n/a

Table V. Volumetric emissions during USG and FSG processing.

5. SUMMARY

Emissions from three Ultima HDP-CVD processes have been determined by quantitative QMS and FTIR measurements. During PSG, USG, and FSG deposition the SiH_4 is fully utilized (0 mg/µm). For FSG films, the SiF_4 emission associated with the deposition step is 7 mg/µm. The NF_3 remote microwave process was shown to effectively eliminate PFC emissions from Ultima HDP-CVD cleaning (3 mg/µm). The MMTCE for this process is 0.15×10^{-9}, which represents a reduction of more than 90 % over current practice. Byproducts of the remote NF_3 clean process were identified as SiF_4, F_2, HF, and unreacted NF_3. Most concern focused on the elemental F_2 generated. A Delatech CDO was found to be very effective at abating the fluorine effluent from the Ultima HDP-CVD processes. The Delatech CDO removes 99.8 % of the influent fluorine.

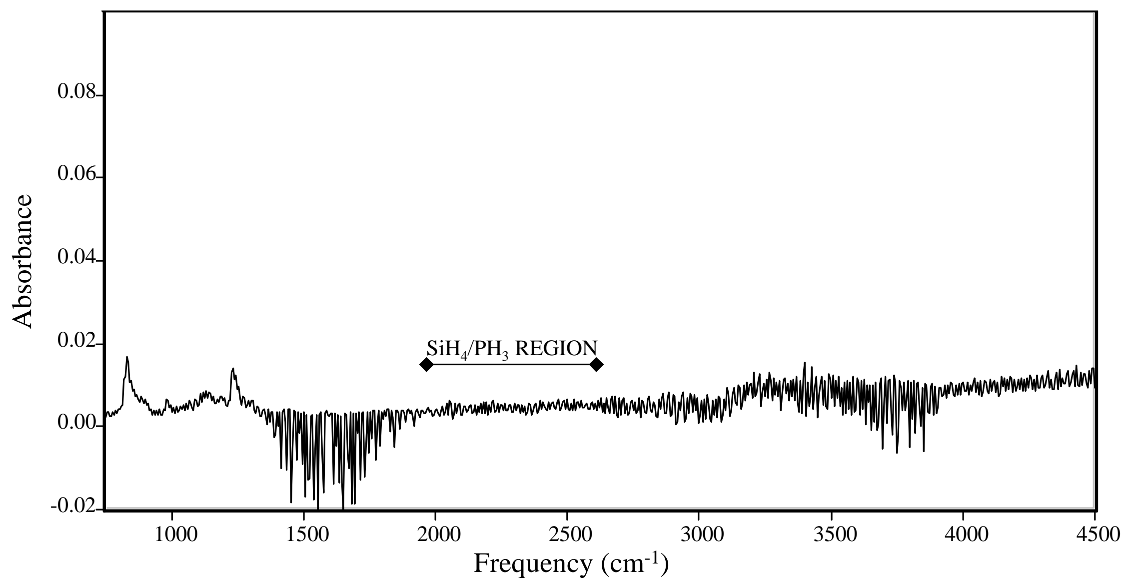


Figure 1.

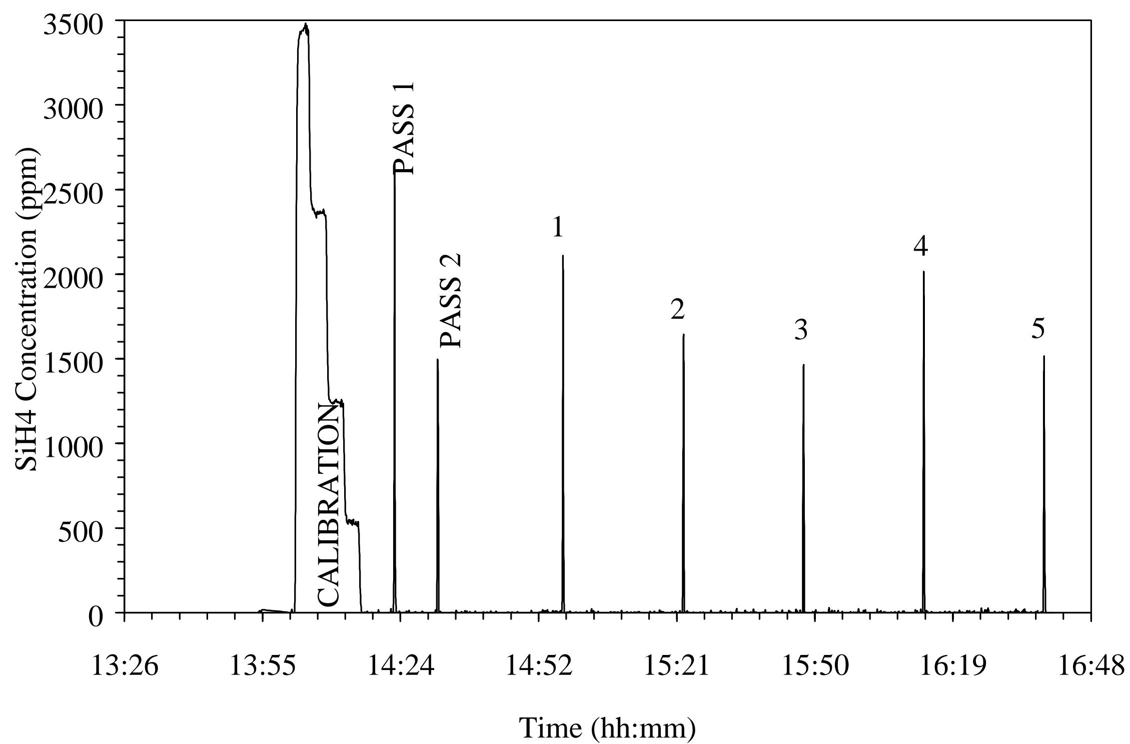


Figure 2.

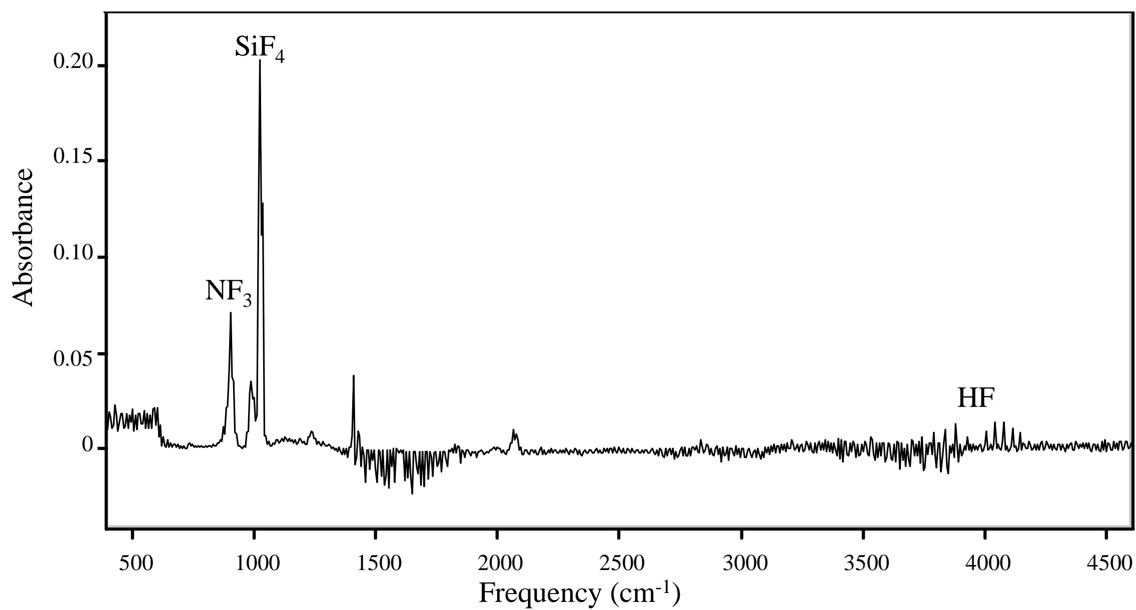


Figure 3.

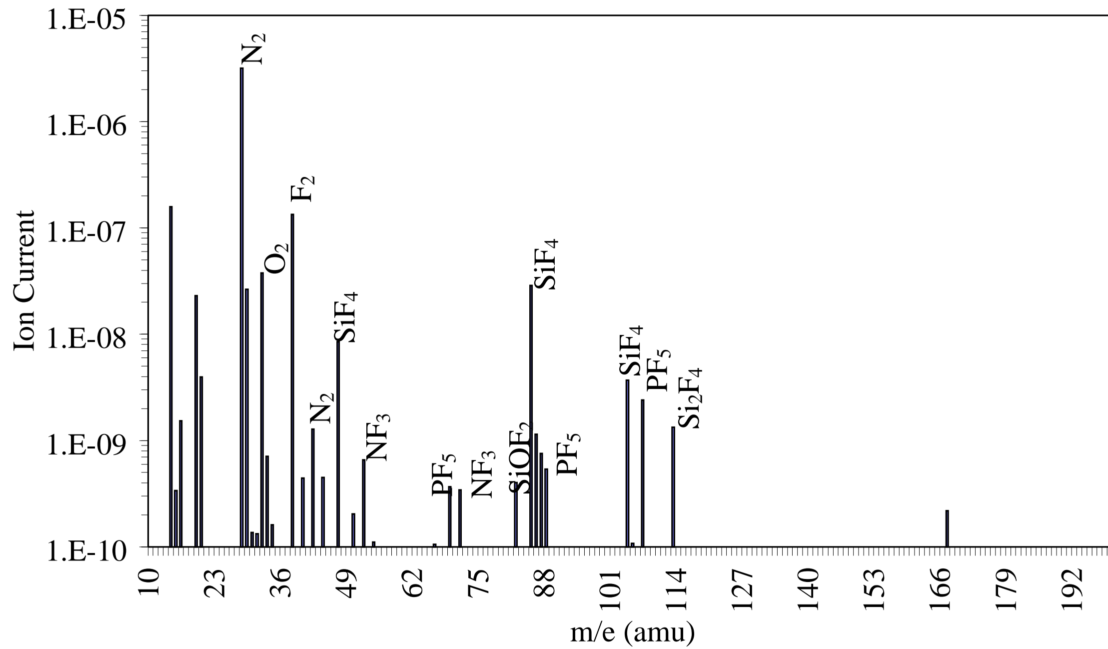


Figure 4.

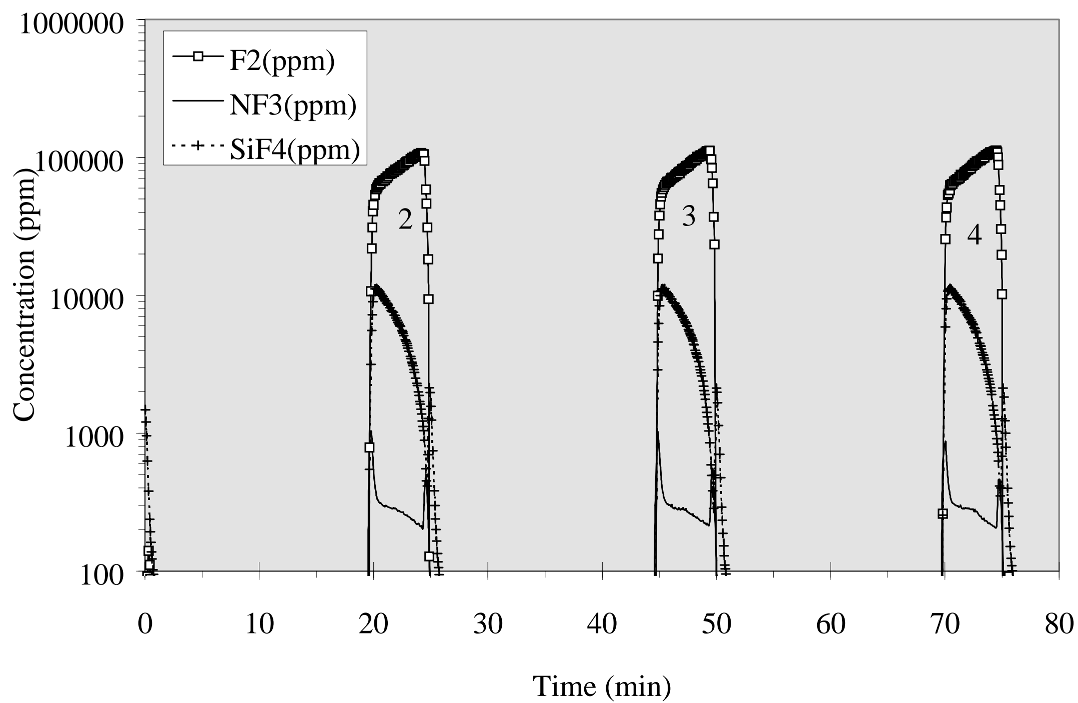


Figure 5.

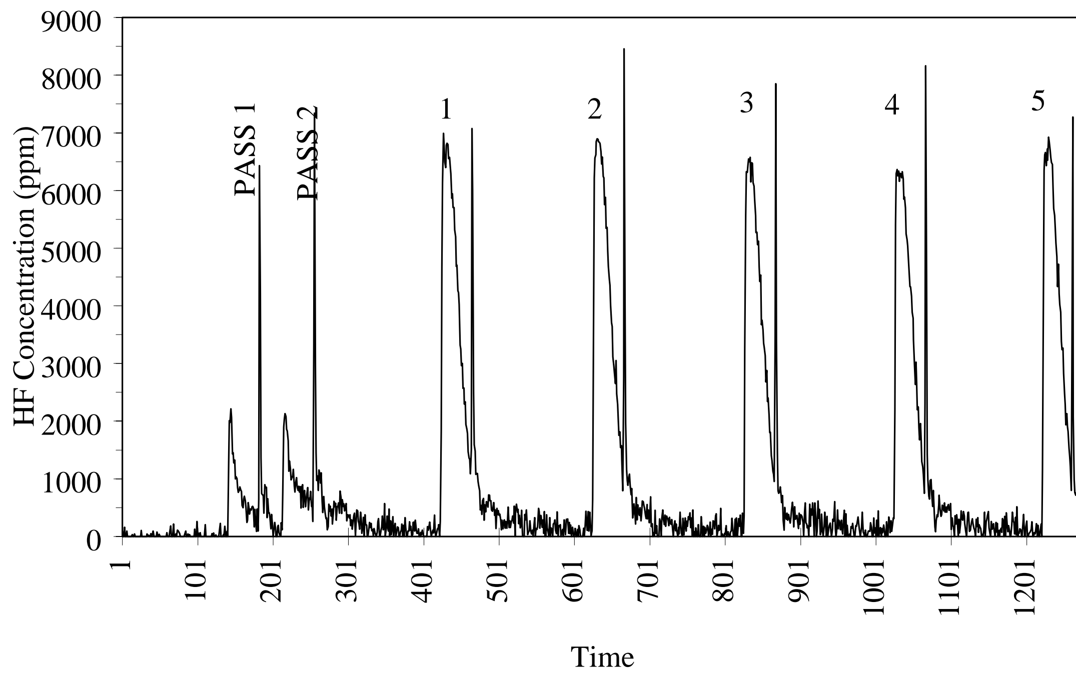


Figure 6.

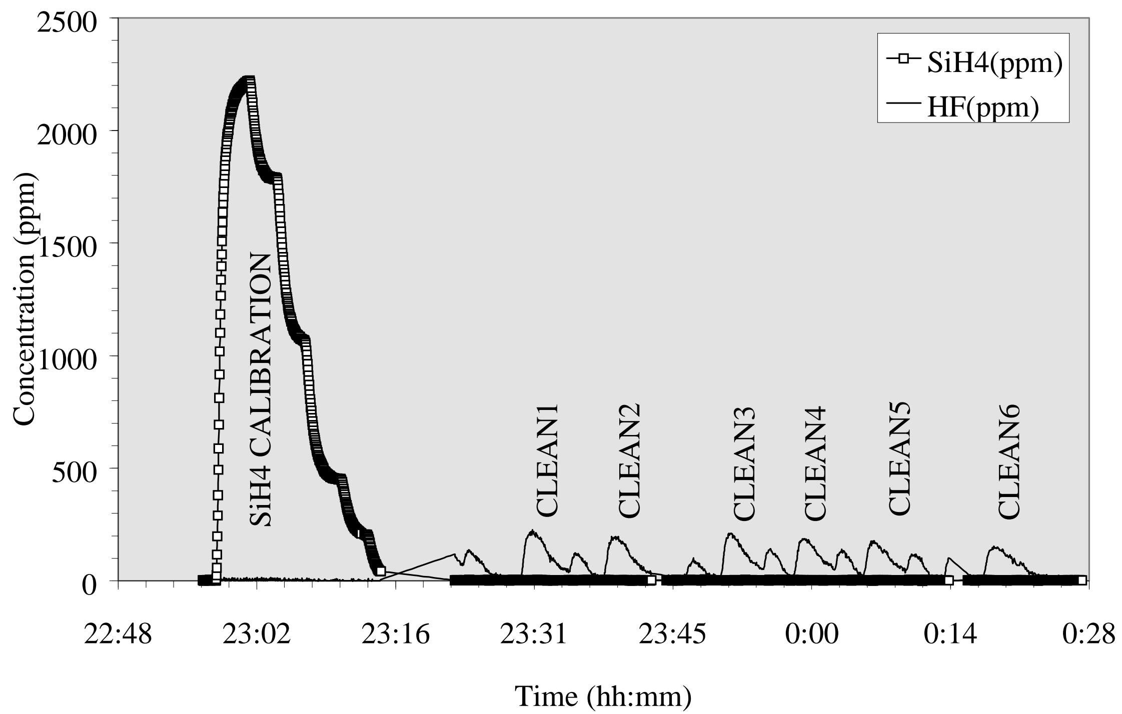


Figure 7.

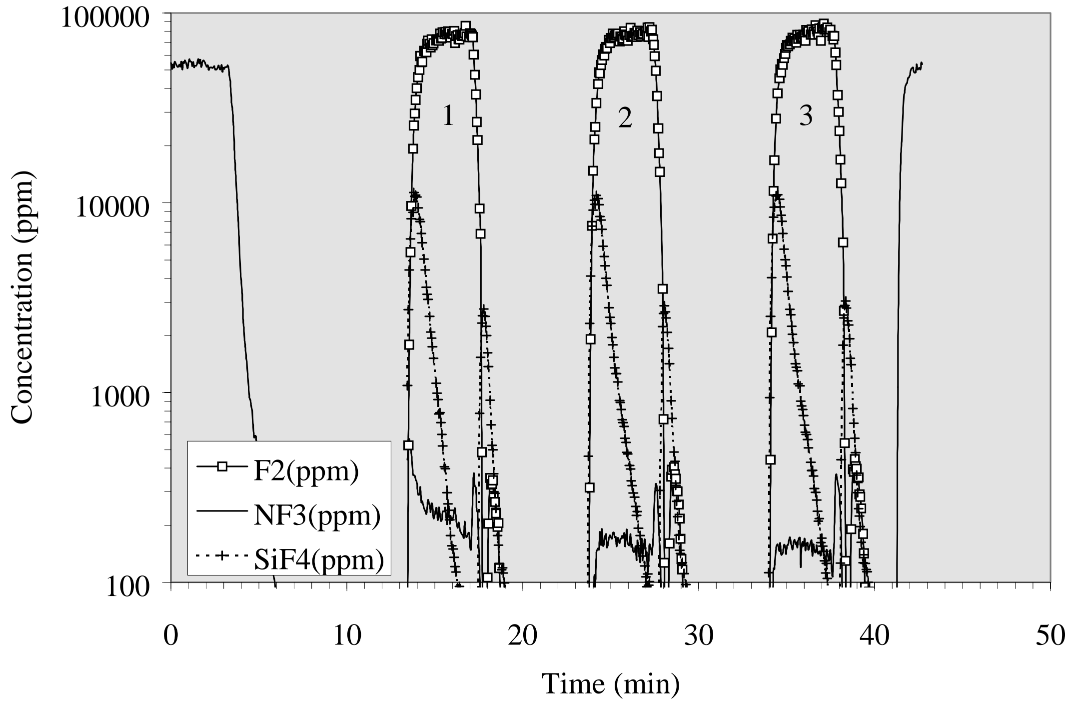


Figure 8.

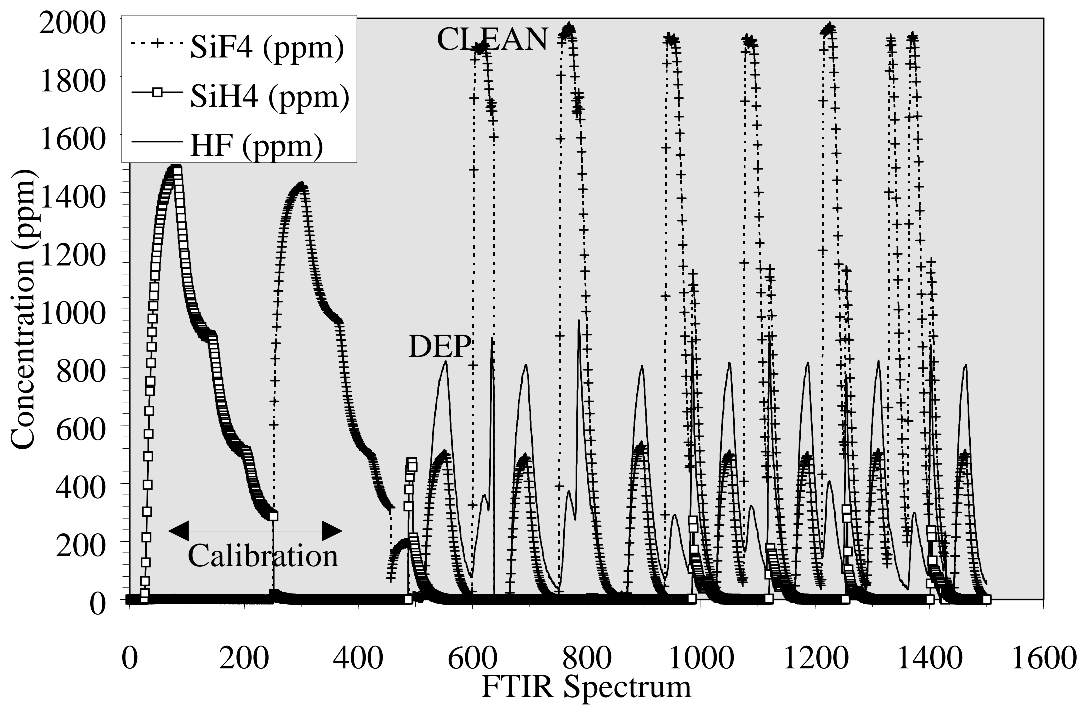


Figure 9.

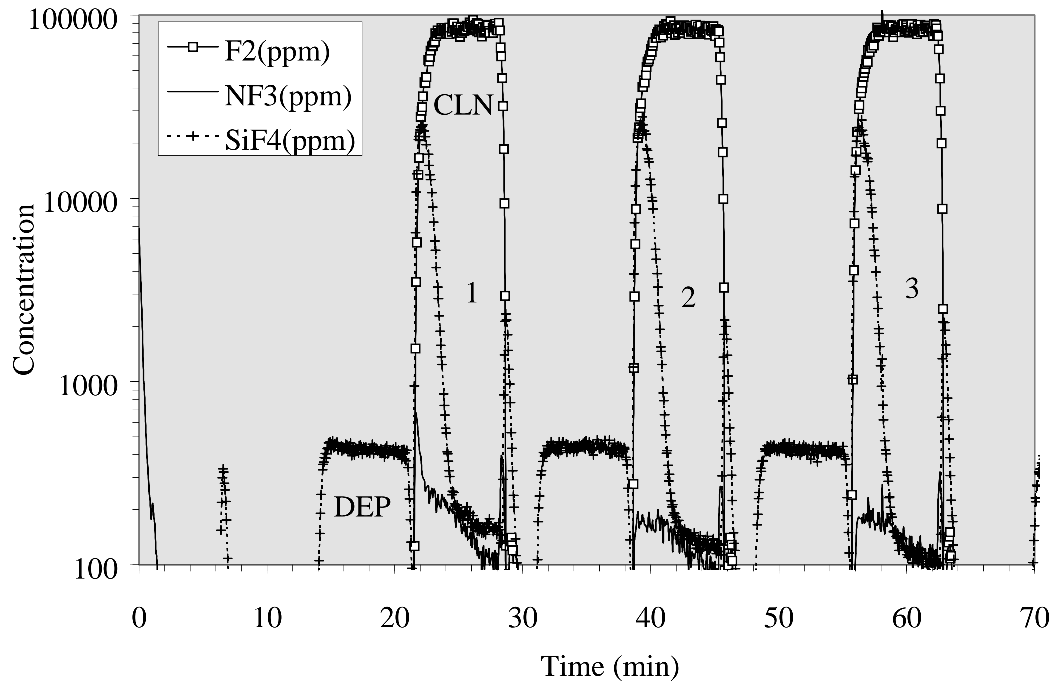


Figure 10.

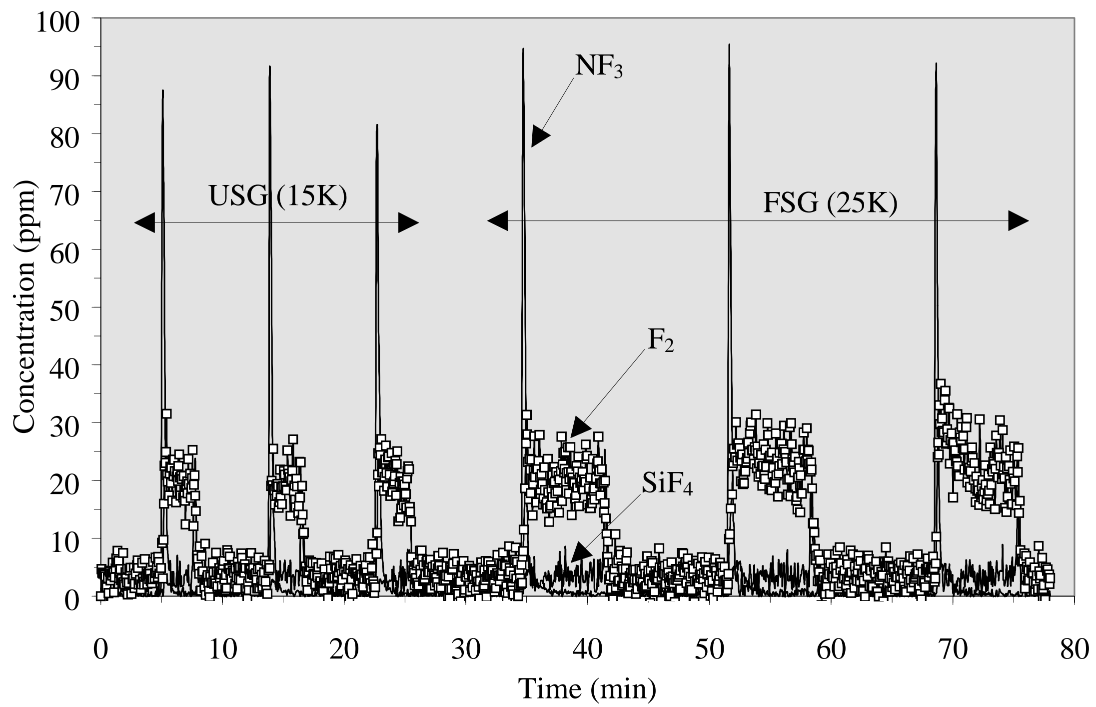


Figure 11.