# **Innovative Surface Wave Plasma Reactor Technique for PFC Abatement**

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Application of surface wave plasmas as an innovative technology for the destruction and removal of perfluorocompounds (PFC) emanating from semiconductor fabrication tools is demonstrated. The destruction of parts per thousand (ppt) concentrations of hexafluoroethane, C<sub>2</sub>F<sub>6</sub>, in oxygen and natural gas mixtures has been investigated as a function of microwave power in a low-pressure plasma reactor at 11.3 Torr. Effluent analysis included the determination of destruction and removal efficiencies (DRE) and product distributions by Fourier transform infrared spectroscopy and mass spectrometry. Destruction and removal efficiences of up to 99.6% for C<sub>2</sub>F<sub>6</sub> were achieved using applied microwave powers from 500 to 2000 W, which corresponded to millisecond range residence times within the plasma. Product analysis indicated that hexafluoroethane conversion was limited to low molecular weight gases such as CO2, CO, COF2, H2O, and HF. CF4 was not produced as a plasma byproduct in any significant quantities. These investigations indicate that surface wave plasma destruction of perfluorocompounds at the point of use is a viable nonintrusive abatement technology for application to semiconductor manufacturing tools.

#### Introduction

It has recently become obvious that there is a discernible human influence on global climate (1). Projections of future global mean temperature change and sea level rise confirm the potential for humanity to alter the earth's climate to an extent unprecedented in our brief history. The long time scales governing both the accumulation of greenhouse gases in the atmosphere and the response of the climate systems to those accumulations mean that many important aspects of climate change are effectively irreversible (2).

Increases in greenhouse gas concentrations since preindustrial times (i.e., 1750) have led to a warming of the earth's surface (See Table 1). The atmospheric concentration of greenhouse gases such as CO2 and CH4 have grown significantly, by about 30% and 145%, respectively (1892-1995). These trends can be attributed largely to human activities such as fossil fuel use. At the present time, some long-lived greenhouse gases particularly PFCs contribute little to global warming, but their projected growth could contribute several percent to warming trends in the next century.

Perfluorocompounds such as C<sub>2</sub>F<sub>6</sub>, CF<sub>4</sub>, C<sub>3</sub>F<sub>8</sub>, and SF<sub>6</sub> are removed very slowly from the atmosphere, and some of these have estimated lifetimes greater than 10 000 years (2). In addition, these perfluorocompounds are excellent absorbers of infrared radiation and thus have very high global warming potentials. As a result, effectively all such emissions accumulate in the atmosphere and will continue to influence the climate for thousands of years. Currently, their concentrations and associated radiative forcings are low but they may become significant in the future if unabated emissions continue.

Perfluorocompounds are vital to the semiconductor industry. The semiconductor industry incorporates numerous low-pressure operations during the manufacturing of semiconductor wafers such as chemical etch, which uses perfluorocompounds. Integrated circuit or computer chip manufacture is a \$50 billion industry and is increasing at a growth rate of 10-15% annually (3). It is estimated that there are approximately 8000 of these tools in the United States and double that number worldwide (3). Typically, gaseous waste streams emanating from these process tools that contain perfluorocompounds are diluted with vast quantities of air or nitrogen and are either released into the atmosphere or thermally incinerated. However, due to the thermal stability of many of these perfluorocompounds such as hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) and tetrafluoromethane (CF<sub>4</sub>), this incineration process is not completely effective, and thus, some of these environmentally harmful compounds are emitted into the atmosphere. Another disadvantage of the thermal incineration method is that the waste streams from numerous tool sets are diluted with nitrogen and combined into a single waste stream prior to incineration. This leads to numerous inefficiencies, because the incinerator must be constantly operated at parameters that give the best results for the bulk flow and not tuned to each individual stream.

The control of greenhouse gas emissions and the reduction of potential global warming which would result are areas of active global interest. Consequently, the semiconductor industry has come under increased pressure to reduce emissions of these compounds to the atmosphere. In response to the U.S. Climate Change Action Plan, the industry is actively evaluating various options such as alternative chemistries, process optimization, recycle and recovery, and abatement. While the first three options may be more desirable from an environmental point of view, the hurdles that have to be overcome for implementation are immense due to the complex nature of the semiconductor manufacturing process. Currently, there are no obvious alternative chemicals to replace perfluorocompounds. Abatement of the emissions at the exhaust of the individual semiconductor manufacturing tools appears to be closest to commercialization and closest to providing a cost-effective solution.

Recently, Bevan et al. have described a new novel plasma device that operates in the radiofrequency range for the destruction and removal of hard to incinerate volatile organic compounds (4, 5). In this paper, we will describe a surface wave plasma device that operates in the microwave region and is extremely efficient for the destruction and removal of perfluorocompounds, which are frequently used for semiconductor etching and cleaning operations. Specifically, we have studied the low-pressure surface wave plasma reactions of hexafluorethane with natural gas and molecular oxygen in a tubular flow reactor as a function of absorbed microwave frequency power. This study includes the determination of

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TABLE 1. Concentrations and Global Warming Potentials (1, 2)

	CO <sub>2</sub>	CH <sub>4</sub>	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	$C_3F_8$
pre-industrial concn	280 ppmv	700 ppbv	zero	zero	zero
concn 1994	358 ppmv	1720 ppbv	72 pptv	2 pptv	zero
rate of concn change (%/yr)	0.4	0.62	2	3.2	NA
atmospheric lifetime (yr)	50-200	12	50 000	10 000	2 600
global warming potential (100 years)	1	21	6 500	9 200	7 000
global warming potential (500 years)	1	6.5	10 000	14 000	10 100

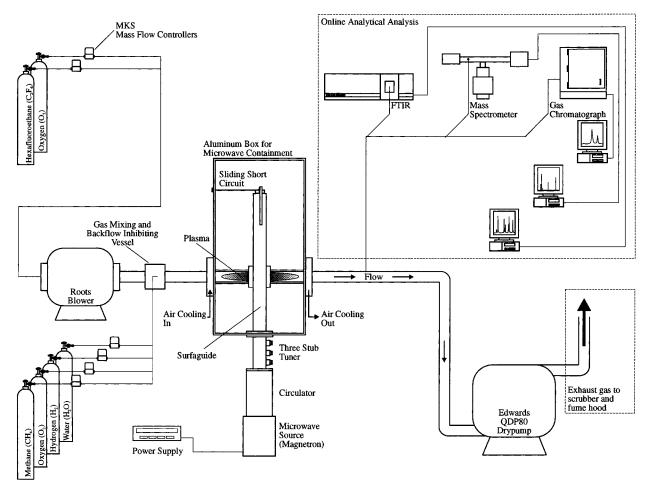


FIGURE 1. Schematic diagram of the surface wave plasma abatement system.

destruction and removal efficiencies for  $C_2F_6$  as well as an in-depth effluent analysis and mass balance.

### **Experimental Section**

The abatement device used in this study is shown in Figure 1. The surface wave high-frequency plasma discharge was produced using a Sairem power supply, a microwave generator at 2.45 GHz, a circulator, a three stub tuner, and a surfaguide surface wave launcher with a sliding short circuit. Semiconductor process gases (C<sub>2</sub>F<sub>6</sub> and O<sub>2</sub>) were metered using MKS type 1179 mass flow controllers at a flow rate of 1 L/min each into a Roots blower vacuum pump. After exiting the Roots blower, these process gases entered a mixing vessel where additive gases were introduced to ensure the complete destruction and removal of hexafluoroethane. Initially, only additional oxygen was introduced into the waste stream. However, the plasma reaction of C<sub>2</sub>F<sub>6</sub> and O<sub>2</sub> produced tetrafluoromethane, CF4, and large quantities of molecular fluorine, F2. CF4 has similar 100- and 500-year global warming potentials and a higher lifetime global warming potential than does C<sub>2</sub>F<sub>6</sub>, so in order to hinder CF<sub>4</sub> formation, we added

natural gas to the simulated waste stream. The addition of a source of hydrogen allows a pathway for HF formation and thus avoids the production of CF<sub>4</sub>. For the duration of this study, the additive gases included additional molecular oxygen (5 L/min) and natural gas (3.6 L/min) which was mostly methane and ethane. These gases were also introduced using MKS type 1179 variable rate mass flow controllers. The mixed gas system was then introduced into a 45 imes 48 mm tubular quartz reactor. This quartz reaction vessel passed perpendicularly through the surfaguide surface wave launcher where a 2-kW short-duration microwave pulse initiated a surface wave plasma within the quartz reaction tube. After ignition, the microwave power supply returned to its preset power level. The coarse microwave circuit tune was accomplished by adjusting the sliding short circuit on the surfaguide launcher. A three stub tuner attached to the input of the surfaguide was then adjusted to maximize the forward power level and minimize back reflections. A circulator was placed between this three stub tuner and the microwave generator to absorb any significant back reflection.

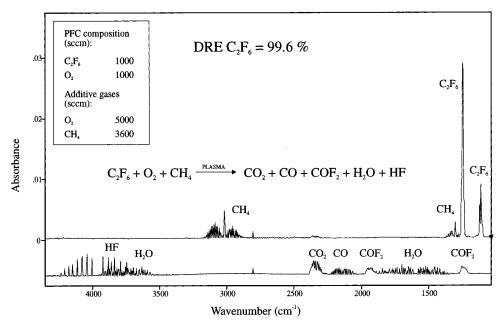


FIGURE 2. FTIR spectra illustrating the surface wave plasma destruction of PFC's.

The inner quartz reaction tube resides inside a larger  $74 \times 79$  mm tubular quartz containment vessel. A 15 scfm stream of compressed air was flowed between this containment vessel and the reactor tube to prevent thermal breakdown. The cooling air entered the system at room temperature and exited the reactor system at 290 °C. The entire plasma reaction system was contained in a Faraday cage. This containment system served two purposes: (1) prevent microwave radiation leakage, which is hazardous to humans, and (2) prevent release of toxic or hazardous gases in the event of catastrophic reaction tube failure. A Neslab recirculating water chiller was used to cool the microwave generator and circulator and the surface wave launcher.

The hexafluoroethane concentration was fixed throughout the study at 94 ppt. We chose 1 L/min  $C_2F_6$  flow because typical recipe flows for  $C_2F_6$  in semiconductor manufacture vary from 200 to 1600 sccm. The molar ratios of the reactants were fixed throughtout this study as

$$1C_2F_6 + 3.6CH_4 + 6O_2 \Rightarrow$$

This yielded concentations of  $C_2F_6=94$  ppt,  $CH_4=340$  ppt,  $O_2=566$  ppt with a total reactor input flow of 10.6 L/min. The overall reactor system was leak checked using the online Leybold Inficon mass spectrometer and kept under low pressure utilizing an Edwards QDP80 dry vacuum pump with a pumping speed of 65 cfm. Product gases exited the dry pump and entered the fume hood where the acid gases were water scrubbed.

Temperature measurements were made 1 m from the microwave applicator. A Chromel-Alumel 304 SS sheath type K 1/4-in. Omega quick disconnect thermocouple assembly was used. A model HH-52 dual input switchable digital thermometer manufactured by Omega Engineering was also employed. Pressure measurements were made using a Leybold Inficon IG3 vacuum gauge.

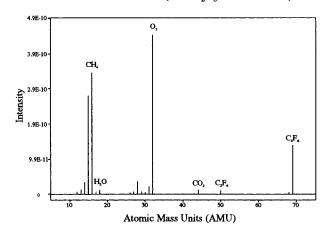
**Product Analysis.** In this work, initial reactant concentrations and final product distributions were determined for various applied microwave powers. Quantative analysis of the plasma reactants and byproducts were performed using a variety of computer-controlled on-line and in situ analytical techniques (see Figure 1). These included gas-phase Fourier transform infrared spectrometry (FTIR) and mass spectrometry (MS). Multiple analytical techniques were employed for an in-depth understanding of the plasma destruction

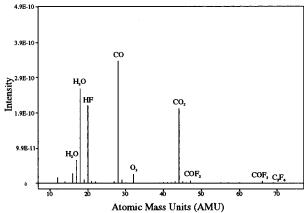
process as well as to critically asses the viability of this technology as a pollution control device for semiconductor process tools.

Quantative gas-phase FTIR was performed using a Biorad FTS-60 spectrometer utilizing a stainless steel heated cell with a path length of 18 cm. A total of 100 co-added spectra were recorded from 500 to 5000 cm<sup>-1</sup> at a resolution of 1 cm<sup>-1</sup>. The spectrometer was equipped with a potassium bromide (KBr) beam splitter and an mecury-cadmiumtelluride (MCT) infrared detector. Again all transfer lines were heated to minimize condensation and avoid adsorption of analytes. Identification of HF, CO, H2O, CO2, CF4, C2F6, and COF<sub>2</sub> was accomplished on the basis of rotational constants, band origins, and by characterizing rotationally resolved vibrational bands of standard reference molecules chosen for calibration purposes. The absorbances of selected rovibrational lines or unresolved rovibrational bands of different concentrations of HF, CO, H<sub>2</sub>O, CO<sub>2</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and COF<sub>2</sub> gases in nitrogen were measured to generate calibration lines for each species. EPA Protocol 1 standard gases were used when available to build a calibration matrix for the FTIR system and to quantitate the observed spectra. The concentrations of these gases in the unknown mixture were determined by matching the absorbances of the selected lines with the calibrated ones. EPA Protocols for the use of Extractive Fourier Transform Infrared Spectrometry for the Analyses of Gaseous Emissions from Stationary Sources formed the basis for FTIR quantitative measurements (6).

Infrared spectra of the plasma destruction of  $C_2F_6$  are given in Figure 2. One spectrum shows the components in the gas stream before plasma application ( $C_2F_6$ ,  $CH_4$ ,  $C_2H_6$ , and  $O_2$ ), and the other spectrum shows the byproducts of the plasma reaction. Oxygen cannot be seen in the infrared spectrum because it is not infrared active. Not only was the destruction and removal efficiency for this experiment high (99.6%), but the process yields only simple, low molecular weight byproducts such as CO,  $H_2O$ ,  $CO_2$ , and other easily scrubbed and neutralized compounds such as  $COF_2$  and HF.

Quantitative mass spectrometry was performed using a differentially pumped in-line Leybold Inficon Transpector 200 AMU residual gas analyzer. This system consists essentially of an ion source, quadrupole mass filter, Faraday cup, and electron multiplier detectors. In-line mass spectrometry was used to sample the product stream at the outlet





 $C_2F_6 + O_2 + CH_4 \xrightarrow{PLASMA} CO_2 + CO + COF_2 + H_2O + HF$ 

FIGURE 3. These mass spectra demonstrate the high DRE and product distribution of the surface wave plasma abatement technology.

TABLE 2. Mass Spectral Cracking Patterns of Interest (8, 9)

		pea	ak 1	peak 2		pe	ak 3	pe	ak 4	peak 5		
compd	mass	m/z	RA	m/z	RA	m/z	RA	m/z	RA	m/z	RA	
C <sub>3</sub> F <sub>8</sub>	188	69	100	31	8.8	169	24.6	50	9.3	119	9	
$C_2F_6$	138	69	100	119	41.3	31	18.3	50	10.1	12	1.5	
CF <sub>4</sub>	88	69	100	50	11.8	19	6.7	31	4.9	25	3.9	
$COF_2$	66	47	100	66	55	28	14	31	4	50	3	
OF <sub>2</sub>	54	35	100	54	62	16	44	19	10			
$CO_2$	44	44	100	16	9.4	28	8.2	12	6.7			
$F_2^-$	38	19	100	38	55							
$O_2$	32	32	100	16	9	28	3					
$C_2H_6$	30	28	100	27	33.6	30	24.1	26	23.5	29	21.2	
CO	28	28	100	12	4.7	16	1.7	29	1.2	14	0.8	
HF	20	20	100	19		1						
H <sub>2</sub> O	18	18	100	17	21							
CH₄	16	16	100	15	85.6	14	17.1	13	8.6	12	2.6	
H <sub>2</sub>	2	2	100	1	2							

of the plasma reactor and to avoid secondary gas-phase reactions. A Welch DIRECTORR vacuum pump differentially pumped the plasma reacted off-gas through a 1/8-in. circular orifice where it held the input pressure to the quadrupole mass spectrometer at 1 Torr. The Transpector 200 AMU residual gas analyzer was equipped with an IPC28 pressure converter which is an orifice system designed to allow the mass spectrometer to sample the gas stream at 1 Torr. Four liters per minute of product gas was pulled through the residual gas analyzer by a Pfeiffer Balzers turbo molecular pump, which was backed by a Leybold Heraus TRIVAC vacuum pump. Sampling pressures in the mass spectrometer were typically  $10^{-5}-10^{-6}$  Torr. As with the FTIR system, standard gases were used to generate calibration curves for the mass spectrometer (7). Mass spectrometric analysis did not reveal the presence of any high molecular weight (C > 1) organic species produced by the plasma reactor.

Figure 3 shows the two mass spectra that were taken simultaneously with the aformentioned FTIR spectra. The first mass spectrum shows the distinct cracking pattern (m/z) for  $C_2F_6$  (69  $CF_3^+$ , 119  $C_2F_5^+$ , 31  $CF^+$ , 50  $CF_2^+$ ),  $O_2$  (32  $O_2^+$ , 16  $O^+$ ),  $C_2H_6$  (28  $C_2H_4^+$ , 27  $C_2H_3^+$ , 30  $C_2H_6^+$ , 26  $C_2H_2^+$ , 29  $C_2H_5^+$ ), and  $CH_4$  (16  $CH_4^+$ , 15  $CH_3^+$ , 14  $CH_2^+$ , 13  $CH^+$ , 12  $C^+$ ). The m/z axis of these spectra were truncated at 70 for visual clarity. The  $C_2F_5^+$  peak resulting from the ionization of  $C_2F_6$  at 119 m/z is not shown. Mass spectral cracking patterns of interest in this experiment are given in Table 2. The first spectrum also shows residual water and carbon dioxide from

previous experiments. The mass spectrometer was located 2 ft from the center of the plasma reactor and is only capable of identifying stable products. The second mass spectrum in Figure 3 shows the plasma byproducts attained by operating the plasma abatement device at 2 kW. When the microwave power is applied, the mass spectral features belonging to  $C_2F_6$ ,  $O_2$ ,  $C_2H_6$ , and  $CH_4$  decrease substantially, and the spectral features due to the plasma byproducts arise. These are  $CO_2$  (44  $CO_2^+$ , 16  $O^+$ , 28  $CO^+$ , 12  $C^+$ ), CO (28  $CO^+$ , 12  $C^+$ ),  $COF_2$  (47  $COF^+$ , 66  $COF_2^+$ , 28  $CO^+$ ), HF (20 HF $^+$ , 19 F $^+$ ), and  $H_2O$  (18  $H_2O^+$ , 17  $OH^+$ ). The possiblity of observing oxyfluorine compounds such as  $OF_2$  and just  $F_2$  was pursued. However, such compounds easily react with the moisture in the effluent stream.

### **Results and Discussion**

Initially, plasma studies were performed to destroy  $C_2F_6$  using only molecular oxygen in a surface wave plasma device. The results of this study are given in Table 3. The simplified unbalanced equation for the plasma destruction of  $C_2F_6$  using additive oxygen is given below as eq 1:

$$C_2F_6 + O_2 \Rightarrow COF_2 + CF_4 + CO_2 + CO \tag{1}$$

The main byproducts of this reaction in order of decreasing concentration are  $COF_2 > CF_4 > CO_2$ :CO under the operating conditions listed in Table 3. The destruction and removal

TABLE 3. Destruction and Removal of PFCs Using Oxygen

			reacta	nts	CF			
microwave power (W)	reactor pressure (Torr)	C <sub>2</sub> F <sub>6</sub> (L/min)	O <sub>2</sub> (L/min)	C <sub>2</sub> F <sub>6</sub> (ppt)	O <sub>2</sub> (ppt)	production (ppt)	emission (L/min)	DRE C <sub>2</sub> F <sub>6</sub> (%)
1950	2.47	1	1	500	500	144.8	0.36	96.5
1950	2.87	1	1.5	400	600	58.5	0.19	97.5
1950	3.21	1	2	333	667	17.8	0.07	98.0
1950	3.52	1	3	250	750	6.4	0.03	98.1
1950	4.26	1	4	200	800	4.3	0.03	95.7
1950	4.72	1	5	167	833	3.2	0.02	84.8
1950	5.33	1	6	143	857	2.3	0.02	70.4

TABLE 4. Destruction and Removal of PFCs Using Oxygen and Natural Gas

microwave power	reactor pressure	reactor temp	residence time	DRE	C <sub>2</sub> F <sub>6</sub>	СН₄	02	CO <sub>2</sub>	СО	COF <sub>2</sub>	CF₄	HF	H <sub>2</sub> O	recov	recovery	
(W)	(Torr)	(K)	(ms)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)	(ppt)	(ppm)	(ppt)	(ppt)	(ppt)	(%)	
0	11.3	298.2	0	0	94	340	566	0	0	0	0	0	0	1000	100	
500	12.2	431.4	2.6	6.5	88	301	510	3.6	30	<1	<1	27	66	1026	103	
1000	17.2	581.2	5.5	29.6	66	223	370	25	71	21	<1	90	153	1019	102	
1500	39.1	773.3	14	92.1	7.5	22	15	115	160	75	<1	219	350	964	96	
1950	43.6	884.6	18.2	99.6	0.35	<1	<1	87	184	58	3.7	279	347	955	96	

efficiences for this process were a function of power and oxygen concentration. DREs varied with oxygen concentration and ranged from 70.4 to 98.1%. However, CF<sub>4</sub> production was also significant at 2–145‰ (0.02–0.36 L/min) depending upon  $O_2$ : $C_2F_6$  ratio. At an applied microwave power of 1950 W, a  $C_2F_6$ : $O_2$  ratio of 1:3 gives the best destruction and removal efficiency (98.1%) for  $C_2F_6$  and the lowest CF<sub>4</sub> production at 6.4 ppt or 0.03 L/min. Since CF<sub>4</sub> is an extremely undesirable byproduct from a global warming perspective, we added natural gas to the reactant mixture to facilitate the destruction and removal process. The addition of a suitable source of hydrogen (CH<sub>4</sub> or H<sub>2</sub>) forms a preferential pathway for the formation of HF, a thermodynamically stable diatomic species that limits the production of other fluorine containing compounds.

The conversion of hexafluoroethane at a fixed input concentration of 94 ppt was studied using different applied microwave powers in a low-pressure (11.3–43.6 Torr) natural gas and oxygen-containing surface wave plasma reactor. The plasma column length was found to increase linearly with applied power and decrease with increasing pressure. See Table 4 for a summary of reactor conditions. Residence times were computed as a function of plasma length and gas velocity. The latter was determined using the following expression ( $\vartheta$ ):

$$v_{\rm f} \, ({\rm m/s}) = 5.31 \times 10^{-9} \left( \frac{QT}{Ap} \right)$$
 (2)

where Q is the total gas flow rate in L/s, A is the cross sectional area of the reactor in  $m^2$ , and T(K) and P(Pa) are the average reactor temperature and pressure. In this study, the latter were approximated to be the ones measured 1 m from the wave launcher and ranged between 431 and 885 K depending on specific reactor conditions. Residence times are also given in Table 4. Residence times were extremely short ranging from 2.6 to 18.2 ms.

This full-scale test was performed on this prototypical abatement system in order to determine its longevity and commercial viability. A simulated tungsten chamber clean source gas supply containing 1 L of hexafluoroethane ( $C_2F_6$ ) and 1 L of oxygen ( $O_2$ ) was flowed into the off-gas abatement sytem where it was mixed with 3.6 L of natural gas, mostly  $CH_4$  and  $C_2H_6$ , and 5 L of oxygen. The mixed feed and waste gas stream were then passsed through the surface wave

plasma abatement system yielding  $CO_2$ , CO,  $COF_2$ ,  $H_2O$ , and HF. The overall experimentally determined balanced chemical equation for the 1950-W plasma destruction of hexafluoroethane is given below in eq 3:

$$1C_2F_6 + 3.6CH_4 + 6O_2 \Rightarrow 1.3CO_2 + 3.2CO + 1COF_2 + 5.2H_2O + 4HF$$
 (3)

This study was performed to determine the destruction and removal as a function of power. The power requirements for total destruction of PFCs are important because the cost of the microwave power supply and generator is by far the most expensive component of the abatement system. Thus, the power requirements for complete abatement of PFCs will determine the commercial viability of this process. In addition, the major byproducts of the reaction were identified and quantitated.

The actual hexafluoroethane destruction and removal efficiencies (DREs) given in Table 4 were determined by averaging independent quantative analyses obtained using the two distinct (FTIR and MS) analytical methods. The FTIR-and MS-determined DREs agreed with each other by less than 0.5% in all cases. We have compared the hexafluoroethane mass density (g/mL) before and after entering the plasma reactor to compute the correspondent DRE from its standard definition (9):

% DRE = 
$$\left(\frac{W_{\rm in} - W_{\rm out}}{W_{\rm in}}\right) \times 100$$
 (4)

where W corresponds to the weight of  $C_2F_6$  in the mixture, and the in and out subscripts denote the quantity before and after being processed. The DREs for the microwave plasma abatement of hexafluoroethane also given in Table 4 are directly proportional to power and residence time. It is also a strong function of the fractional composition of the waste stream to be treated. The waste stream composition (process gases + additive gases) used in this study was empirically determined to be optimal for maximum destruction efficiency as well as designed to produce the desired byproducts. In previous studies, excess oxygen was added to abate  $C_2F_6$ . However, this process yielded  $CF_4$  as a byproduct.  $CF_4$  is known to have a higher lifetime global warming potential than does  $C_2F_6$ , the compound we were trying to abate. Thus,

we decided to use additive gases such as  $CH_4$  or  $H_2$  to promote the formation of HF and to optimize the simultaneous destruction and removal of  $CF_4$ . The extent of abatement is also a complex function of the reactor pressure that is related to inlet stream compostion and pumping speeds. Thus, the efficiency of the reactor increased with increasing applied microwave power and resulted in relatively large pollutant removals (99.6%) when utilizing only 2 kW of incident microwave power with a residence time of only 18.2 ms.

The product distributions from selected 500, 1000, 1500, and 2000 W trial run analyses are summarized in Table 4. These numbers are the average of the FTIR- and MSdetermined concentrations where applicable. The FTIR- and MS-determined concentrations agreed with each other to within 5% except for perfluorocompounds, which agreed to within 1%. Not only is the destruction and removal efficiency high, but the process also yields only simple, low molecular weight byproducts. The striking simplicity of the species produced by the plasma reaction (diatomic and triatomic molecules) is in contrast to previously reported nonequilibrium plasma studies. Hollahan (12) described the reactions of saturated and unsaturated organic substances with hydrogen and oxygen leading to a wide product distribution of nonparent hydrocarbon species. This has been corroborated by Barat and Bozzelli (13) in their low-pressure reactions of chlorinated hydrocarbons under reducing and oxidizing conditions. The main products of the surface wave plasma destruction are either relatively harmless (CO2, CO, H<sub>2</sub>O) or easily scrubbed and neutralized products (HF and COF<sub>2</sub>). The mass recoveries for these trial runs were high at 96% and can be attributed to the use of multiple analytical methods and techniques.

The product distributions resulting from the surface wave plasma reactions that we have investigated are likely to stem from both thermal and nonthermal processes. During the nonthermal stage, the species travel throughout the plasma zone and are subjected to a number of electron collisions in a time range of 1-10 ms. Unlike plasma processes occurring in the few Pa pressure range, the neutral gas temperatures within the plasma at the reactor pressures used in our investigation are estimated between 1000 and 2000 K depending on the power applied, reactor pressure, and gas composition (14). Thus, in the second stage, the stable and intermediate species generated in the first stage experience a fast cooling (ca. 100 K/ms) as they exit the plasma volume. The resulting short residence times are likely to limit the number of slow multistep mechanisms that are essential in the formation of more complex nonparent fluorohydrocarbon

In conclusion, this study demonstrates the feasibility and advantages of utilizing low-pressure surface wave plasmas to destroy and remove thermally stable gases such as hexafluoroethane emanting from semiconductor fabrication tools. The reactor has been shown to efficiently destroy  $C_2F_6$  under conditions of low residence times, applied microwave

powers, and pressures. Moreover the process does not require the addition of expensive rare gases nor preheating of the reactant gas mixture. The byproducts of this abatement device are all simple, low molecular weight compounds. The hazardous byproducts can be easily water scrubbed. This abatement device was also successful in the abatement of CF<sub>4</sub>, NF<sub>3</sub>, and C<sub>3</sub>F<sub>8</sub> with the aformentioned additive gases (oxygen, natural gas, and hydrogen). In addition, as expected in these oxygen-rich conditions, we did not observe any soot formation within the reactor walls that would hinder continuous operation. These aforementioned characteristics make surface wave discharges an attractive alternative to thermal incinerators for the destruction and removal of hard to incinerate gases emanating from industrial processes operating under low pressures such as semiconductor fabrication tools.

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