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Surface Wave Plasma Abatement of CHF_3 and CF_4 Containing Semiconductor Process Emissions

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Projected exponential growth in semiconductor device manufacture over the next few years demands technology to reduce the corresponding increase in etchants such as perfluorocompounds (PFCs), CHF_3, and SF_6 that would be emitted into the atmosphere. These compounds are a cause for concern because of their large global warming potentials relative to CO_2 and of their long lifetimes in the atmosphere, often tens of thousands of years. We demonstrate that a plasma-based technology can yield effective (up to 99.9%) destruction and removal efficiencies (DREs) for CF_4 and CHF_3 present in etch recipes widely used in the semiconductor industry. Specifically, we report application of surface wave plasmas at 2.45 GHz for this purpose. Post-plasma effluent analysis included the determination of DREs and product distributions, simultaneously by gas-phase FTIR and QMS. Application of microwave powers from 500 to 1950 W were investigated and DREs for CF_4 and CHF_3 reported. Final product analysis indicated that PFC conversion was limited to low molecular weight gases such as CO_2, CO, COF_2, H_2O, and HF. These investigations demonstrate that surface wave plasma destruction of the referenced PFCs at the output of semiconductor etch tools is a viable nonintrusive point of use abatement technology.

Introduction

The effects of global warming on climate change has recently created great interest and concern (*1*). During the Third Conference of the Parties (COP3) held December of 1997 in Kyoto, Japan, 171 countries developed a treaty that will restrict emissions of the six most prominent greenhouse gases (*2*). These compounds, listed in decreasing atmospheric concentration, include: CO_2, CH_4, N_2O, hydrofluorocarbons (HFCs), PFCs, and SF_6. The forced global warming due to CH_4, N_2O, and especially CO_2 was the major focus of early attention. Since the Kyoto conference, it is now recognized that there could be significant climate impact due to the emissions of HFCs, PFCs, and SF_6 as well.

Perfluorocompounds (i.e., C_2F_6, CF_4, and C_3F_8) and sulfur hexafluoride (SF_6) are vital to the semiconductor manufacturing industry (*3*). These chemical species serve as the precursors of atomic fluorine which is used in a variety of silicon wafer etch and chamber clean applications. PFCs themselves are typically nonreactive under ambient conditions but are broken down in the plasma reactor chambers used for device manufacturing. Ordinarily, only 20−40% of the perfluorocompounds are actually consumed during an etch process (*3*, *4*). The residual gases are subsequently evacuated from the process chambers, passed through a variety of exhaust treatment systems to remove the corrosive components, and are then released to the atmosphere. Due to their chemical inertness, the unused perfluorocompounds are unaffected by these treatment systems and are thus emitted into the atmosphere. The problem with PFCs is that they have considerable atmospheric lifetimes and are very efficient absorbers of infrared radiation (*1*).

Although any global warming attributable to PFCs is currently low, for example atmospheric CF_4 concentrations in 1994 was 72 parts per trillion (ppt), it is now recognized that this situation could significantly change soon (*1*). Semiconductor device manufacturing is projected to increase at an exponential rate over the next few years (*5*). All PFC emissions will continue to accumulate in the atmosphere and will have influence on the global climate for tens of thousands of years. At this time there are no alternative chemicals to replace PFCs and their abatement at the exhaust of the individual semiconductor tool appears to be the only available near-term solution.

This paper is concerned with the effective abatement of trifluoromethane and tetrafluoromethane, CHF_3 and CF_4, using microwave-generated surface wave plasmas. Both CHF_3 and CF_4 are used in mixtures to simulate a variety of etch process recipes. The work presented in this paper will demonstrate that surface wave plasmas are capable of destroying and removing these perfluorocompounds in simulated semiconductor process streams with >99% efficiency. CF_4 in particular has been extensively used for semiconductor manufacturing processing but has proven to be particularly difficult to destroy and remove (*4*). In many respects, CF_4 is the prototypical PFC to abate because of its chemical thermal stability due to the strong covalent nature of its bonding. Its C−F bond strength (*6*) is approximately 112−116 kcal mol^{-1}. We shall demonstrate that surface wave plasma technology is particularly effective for point-of-use semiconductor etch emissions. It is well-known that such plasmas are capable of high electron densities and nonequilibrium conditions, having high electron temperatures (5000−10000 K) but low local thermodynamic equilibrium temperatures (*7*). We shall exploit such conditions to initiate the electron dissociation and other processes that can convert the PFCs involved into reactive intermediates such as CF_3 and CF_2 (*3*, *8*, *9*).

Such intermediates have lower activation energies and proceed to react with pre- and post-plasma additive gases such as H_2 and O_2, thus producing simple final byproducts such as CO_2, CO, COF_2, H_2O, and HF, which greatly reduce the global warming effects of the original PFCs. The COF_2 and HF can be water-scrubbed and neutralized. This simple and cost-effective approach has not been previously exploited in the semiconductor industry. It avoids difficulties associated with other alternative approaches such as recycle/recovery or benign chemical approaches that have so far proven ineffective and will take years to develop (*10*). Specifically, we shall demonstrate that this technology is capable of destroying and removing CF_4 and CHF_3 in simulated semiconductor process streams with >99.9% efficiency.

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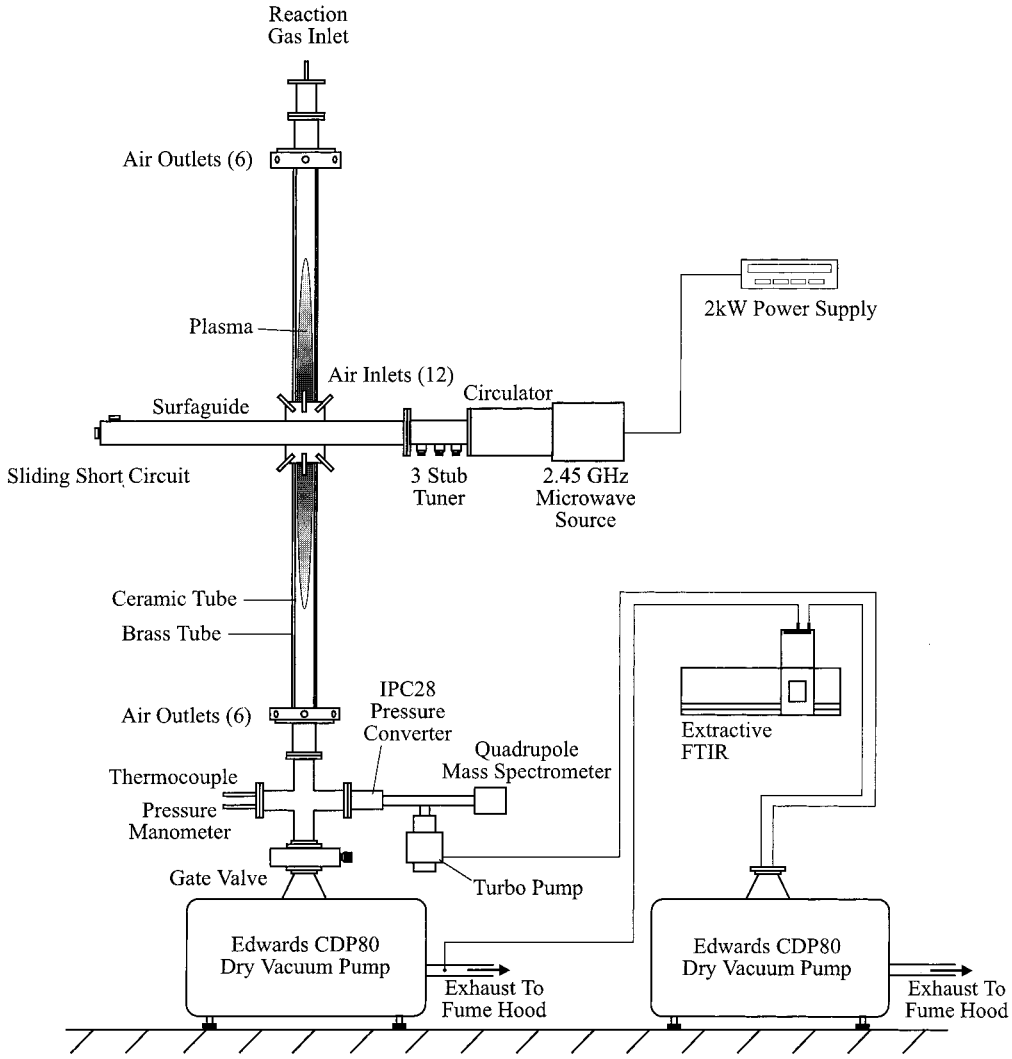

FIGURE 1. Schematic diagram of the surface wave plasma abatement system.

Experimental Section

The application of high-frequency surface wave plasmas (SWPs) for the abatement of C_2F_6 has been described in our previous work (*11*, *12*). A schematic representation of this system including the on-line analytical instrumentation used to characterize the inlet and outlet stream compositions is shown in Figure 1. The plasma discharge is produced within a 5 foot long by 3 in. diameter ceramic tube using a 2 kW Sairem power supply, 2.45 GHz microwave generator, circulator, three-stub tuner, and a surfaguide surface wave launcher having a sliding short circuit. The AC power to microwave energy conversion is approximately 60% by direct measurement. It is expected that the microwave to plasma energy coupling is in excess of 90% (*7*). The analytical instrumentation included a differentially pumped in situ Leybold Inficon Transpector 200 RGA mass spectrometer and an extractive Bomem 9100 FTIR having a 1 to 10 m adjustable path length heated stainless steel gas cell.

Laboratory experiments were conducted in which the surface wave plasma device was used to destroy PFCs from simulated semiconductor process streams. Three centerline etch process recipes and a fourth CF_4 recipe, with their component flow rates in standard cubic centimeters per minute (sccm), are given

etch recipe	additive gases		
$5CF_4 + 50CHF_3 + 60Ar$	$\Rightarrow 60H_2 + 60O_2$	$\Rightarrow$ plasma device	(1)
$94CF_4 + 26CHF_3 + 480Ar$	$\Rightarrow 60H_2 + 60O_2$	$\Rightarrow$ plasma device	(2)
$5CF_4 + 50CHF_3 + 60Ar$	$\Rightarrow 60H_2 + 60O_2 + 40N_2$	$\Rightarrow$ plasma device	(3)
$55CF_4 + 60Ar$	$\Rightarrow 110H_2 + 110O_2 + 40N_2$	$\Rightarrow$ plasma device	(4)

The total flow rate varied from 235 to 720 sccm with corresponding pressures between 280 and 500 mTorr. Additive hydrogen and oxygen were used to react with the PFCs in the plasma medium, thus preventing their reformation by forming HF and CO_2 as stable byproducts. Also, recipes 3 and 4 each contained 40 sccm of dry nitrogen, N_2. Nitrogen is used as purge gas for the turbo molecular pumps that evacuate the semiconductor process etch chambers. Some experiments were therefore conducted with nitrogen added as part of the simulated process stream in order to detect for the possible formation of nitrogen oxides, i.e., NO_x. Trials were conducted in which the initial reactant concentrations and relative final product distributions were determined as the applied microwave power was increased from 500 to 1950 W using approximately 500-W increments.

MKS type 1179 mass flow controllers having adjustable flowrates of 0−200 and 0−1000 sccm were used to control the individual components of the simulated etch process recipes. The simulated recipes and additive gases were introduced into a 3″ o.d. tubular ceramic reactor that

TABLE 1. Destruction and Removal of PFCs[a]

	destruction and removal efficiencies for the plasma abatement of tetrafluoromethane									
recipe no.	CHF_3 (sccm)	CF_4 (sccm)	Ar (sccm)	O_2 (sccm)	H_2 (sccm)	N_2 (sccm)	pressure (mTorr)	*T* (F)	power (W)	CF_4 DRE (av) (%)
1	50	5	60	60	60	0	310	116	500	86.0
1	50	5	60	60	60	0	312	147	1000	98.2
1	50	5	60	60	60	0	315	119	1500	99.0
1	50	5	60	60	60	0	315	90	1950	99.1
2	26	94	480	60	60	0	480	173	500	35.3
2	26	94	480	60	60	0	490	452	1000	66.4
2	26	94	480	60	60	0	495	483	1500	87.8
2	26	94	480	60	60	0	500	500	1950	94.6
3	0	55	60	110	110	40	302	101	500	59.5
3	0	55	60	110	110	40	324	109	1000	92.2
3	0	55	60	110	110	40	329	110	1500	99.3
3	0	55	60	110	110	40	329	113	1950	99.8
4	50	5	60	60	60	40	282	95.2	500	95.7
4	50	5	60	60	60	40	286	97.2	1000	99.5
4	50	5	60	60	60	40	286	97.4	1500	99.7
4	50	5	60	60	60	40	287	97.5	1950	99.7

[a] As stated in the text, DRE measurements by FTIR and mass spectrometry agreed to within 0.5%. Therefore, we report our DRE errors as being ±0.5%.

$$5\ CF_4 + 50\ CHF_3 + 60\ Ar + 60\ O_2 + 60\ H_2 + 40\ N_2 \xrightarrow[1500\ Watts]{PLASMA} HF + CO_2 + CO + COF_2 + H_2O$$

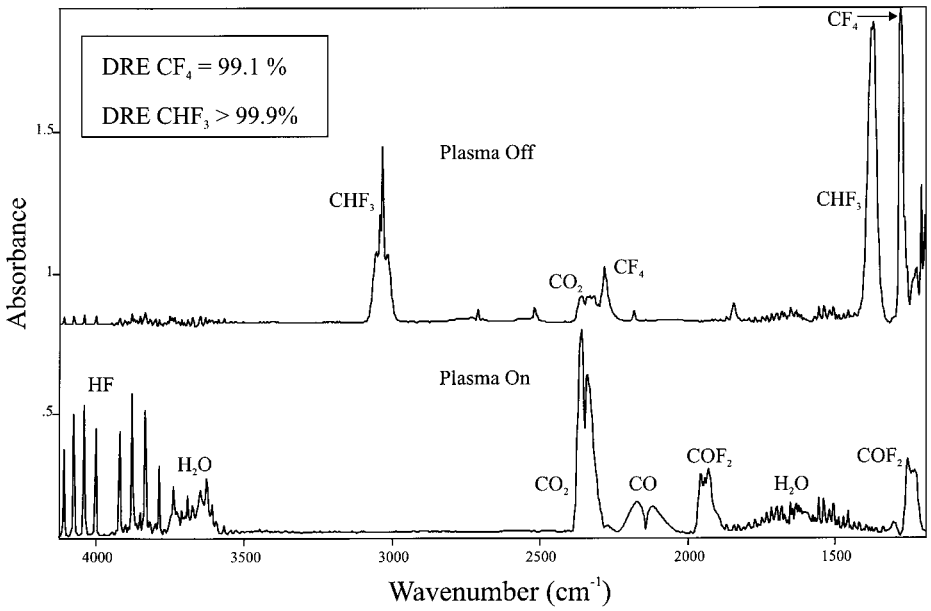

FIGURE 2. FTIR spectra illustrating the surface wave plasma destruction of 5 sccm of CF_4 and 50 sccm of CHF_3 from recipe 1.

perpendicularly intersects the surfaguide surface wave launcher. To ignite the plasma, a 2-kW short duration microwave pulse is applied to the gaseous medium. After ignition, the microwave power supply automatically returns to its preset power level and the plasma remains lit. To coarsely tune the microwave circuit a sliding short circuit was used. A three-stub tuner was then used for fine-tuning by optimizing the forward power/reflected power conditions. A circulator device located between the three-stub tuner and the microwave generator absorbed any significant back reflected microwave radiation. Also depicted in Figure 1, the ceramic plasma tube resides inside two 3.5″ i.d. brass tube segments and was cooled by 15 standard cubic feet per minute (scfm) of compressed dry air passed between this containment vessel and the reactor tube. Under normal operating conditions, the cooling air entered the system at room temperature and exited the reactor system at 40−100 °C. A Neslab recirculating water chiller, model CFT-75, was used to cool the microwave generator, circulator, and the surface wave launcher. Plasma temperature measurements were made 1 m from the microwave applicator using a $^1/_4$″ Omega Chromel-Alumel 304 SS thermocouple which was inserted into the process vacuum line. An Omega Model HH-52 dual input digital thermometer displayed the temperature. Pressure measurements were made using a Leybold Inficon IG3 vacuum gauge and two capacitance manometers having ranges of 0−1 and 0−10 Torr. An Edwards CDP80 dry vacuum pump having a pumping speed of 65 scfm provided the roughing vacuum and the product gases were exhausted to a fume hood where the corrosive gases were water scrubbed and neutralized.

Quantitative IR measurements were obtained using a Bomem 9100 FTIR equipped with a potassium bromide (KBr) beam splitter, a room-temperature DTGS infrared detector,

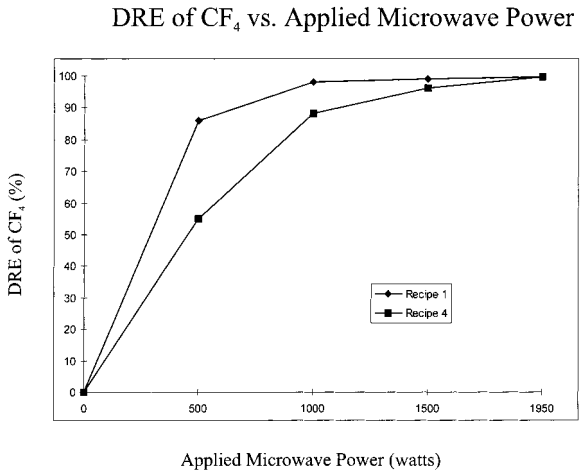

FIGURE 3. Destruction and Removal Efficiency (DRE) plotted as a function of applied microwave power for recipes 1 and 4.

and a 1 to 10 m adjustable path length stainless steel heated gas cell. An extractive sampling method was used in which the plasma byproduct gases were collected from the exhaust of the roughing vacuum pump. All transfer lines were heated to minimize condensation and all infrared spectra were recorded at atmospheric pressure. For each infrared analysis 100 scans were co-added to yield a final spectrum encompassing the region of 500−5000 cm^{-1} at 1 cm^{-1} resolution. Identification of the byproduct gases including HF, CO, H_2O, CO_2, CF_4, CHF_3, and COF_2 was accomplished on the basis of rotational constants and band origins and by characterizing the same features of standard reference molecules chosen for calibration purposes. Calibration matrices for each species were generated by measuring the absorbances of selected rovibrational features of different concentrations of each gas diluted in nitrogen. EPA Protocol 1 standard gases were used when available to build a calibration matrix for the FTIR system and quantitate the observed spectra. The concentrations of these gases in the byproduct exhaust were determined by matching the absorbances of the selected lines with the calibrated ones (*13, 14*).

Quantitative mass spectrometry was performed using a differentially pumped in situ Leybold Inficon Transpector 200 RGA Mass Spectrometer. Sampling of the plasma byproduct gases was conducted on-line orthogonal to the vacuum foreline before the roughing vacuum pump. Thus, the mass spectrometer sample gases were not diluted with nitrogen purge gas as was the case in the FTIR measurements. The components of this system included an ion source, a quadrupole mass filter, a Faraday cup/electron multiplier detector, and a Pfeiffer Balzers turbo molecular pump. Differential pumping was accomplished using a second Edwards CDP80 dry vacuum pump that sampled the plasma byproducts through a $^1/_8$ in. circular orifice. This differential pumping scheme kept the inlet pressure to the mass spectrometer constant for a given set of experiments. The mass spectrometer itself used a Leybold Inficon IPC28 pressure converter that allowed the mass spectrometer to sample pressures as high as 1 Torr. Pressures within the mass spectrometer were typically 10^{-7} Torr. As previously explained for the FTIR system, standard gases were used to generate calibration curves for the mass spectrometer, as well.

Results and Discussion

Studies were performed to investigate the destruction of CF_4 and CHF_3 for etch recipes 1−4 using additive molecular oxygen and hydrogen and using different applied microwave powers. As in previous work (*11*), the performance of the surface wave plasma (SWP) abatement device is described in terms of a destruction and removal efficiency (DRE). This value describes the percentage of the perfluorocompound that has been destroyed and its standard definition is given as (*15*)

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

where the W_{in} and W_{out} denote the quantity of the specific perfluorocompound before and after application of the plasma. Table 1 gives the results for the determination of the DREs of the tetrafluoromethane and trifluoromethane components. These were determined by averaging independent

$$55\ CF_4 + 60\ Ar + 40\ N_2 + 110\ O_2 + 110\ H_2 \xrightarrow[1950\ \text{Watts}]{\text{PLASMA}} HF + CO_2 + CO + COF_2 + H_2O$$

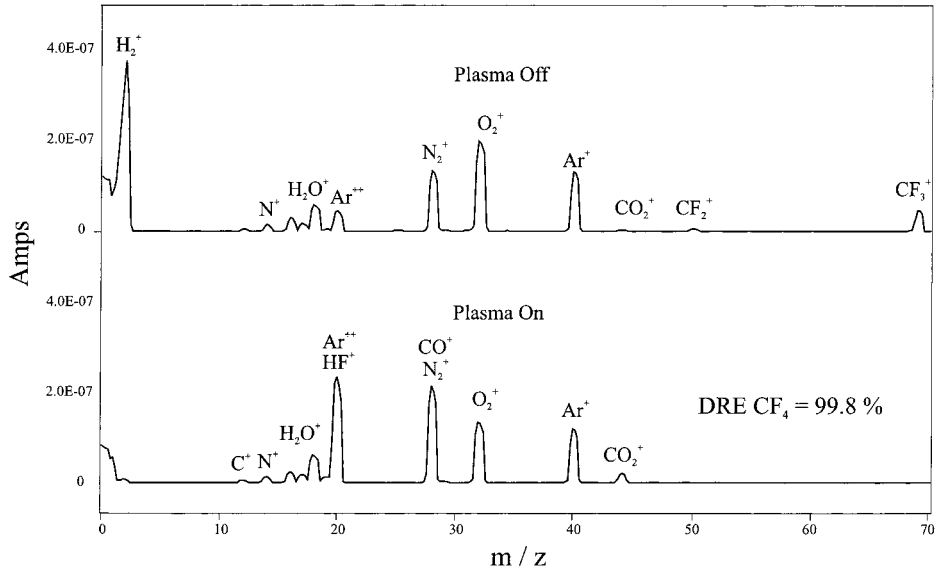

FIGURE 4. Mass spectra illustrating the surface wave plasma destruction of 55 sccm of CF_4 from recipe 4.

TABLE 2. Plasma Product Distribution and Mass Recovery[a]

microwave power (W)	DRE CHF_3 (%)	DRE CF_4 (%)	products									mass recovery (%)
			CO_2 (ppm)	CO (ppm)	COF_2 (ppm)	CH_3 (ppm)	CF_4 (ppm)	HF (ppm)	H_2O (ppm)	H_2 (ppm)	O_2 (ppm)	
1000	99.999	99.658	541	1177	285	0.03	6.34	5316	296	0	705	95
1950	>99.9999	99.843	532	1193	260	0	0.29	5431	296	0	756	96

[a] Errors in the end product concentrations on average are ±1%.

quantitative analyses using the two distinct (FTIR and MS) analytical methods. The DREs determined by these two methods agreed with each other to better than 0.5% in all experiments.

Figure 2 shows two FTIR spectra, demonstrating the application of the SWP system to the components of etch recipe 1. The upper trace reveals the ν_1 and ν_4 infrared absorptions for CHF_3 (50 sccm) and the ν_3 absorption for CF_4 (5 sccm). The lower trace shows the infrared absorptions for the byproducts from a 1500-W plasma that included HF, H_2O, CO_2, CO, and COF_2. For tetrafluoromethane, the absorbance area was determined in each spectrum thus giving W_{in} and W_{out}. With the use of these values, it was determined that a DRE of 99.1% was obtained for this recipe, using only 1500 W. DREs for trifluoromethane were greater than 99.9% in all experiments, even when using only 500 W of applied power. CHF_3 is more easily destroyed than CF_4 because the C−H bond strength is 98 kcal mol^{-1} as opposed to the C−F bond energy (*6*), which is 116 kcal mol^{-1}. Thus, the C−H bond is more easily broken, and once produced, the remaining CF_3 fragment is easily destroyed within the plasma medium. Figure 3 charts the destruction and removal efficiency of CF_4 versus applied microwave power for recipes 1 and 4. Clearly, the DRE of CF_4 increases with microwave power and at 1950 W (50 W were back-reflected) the DREs were 99.1% and 99.8% respectively for recipes 1 and 4.

In Figure 4, mass spectra are shown that further illustrate the performance of the SWP for destroying PFCs. In the upper trace is the spectrum obtained before the plasma was applied to the pure CF_4 recipe 4. One can see the distinct patterns (*16*, *17*) (m/z) for CF_4 ($69CF_3^+$:$50CF_2^+$), O_2 ($32O_2^+$:$16O^+$), H_2 ($2H_2^+$:$1H^+$), N_2 ($28N_2^+$:$14N^+$), and Ar ($40Ar^+$: $20Ar_2^+$). When the microwave power is applied, as seen in the lower trace, the spectral features arising from CF_4, O_2, and H_2 decrease substantially and the features due to the plasma byproducts arise. These are CO_2 ($44CO_2^+$:$16O^+$:$28CO^+$:$12C^+$), CO ($28CO^+$:$12C^+$), HF ($20HF^+$:$19F^+$), and H_2O ($18H_2O^+$:$17OH^+$). Here one can see that the CF_3^+ almost completely disappears, but a measurement of the residual CF_3^+ can still be made. In this case, as with the FTIR measurement, it was determined that the DRE of a process mixture having 55 sccm of CF_4 was 99.8%.

Table 1 contains the gas flows, reaction pressures and temperatures, applied microwave power levels, and destruction and removal efficiencies for CF_4. As can be seen, the DREs for tetrafluoromethane are directly proportional to power and the fractional composition of the waste stream to be treated. The extent of abatement is also a complex function of the reactor pressure which is related to inlet stream composition and pumping speeds. Table 2 lists the results obtained for a plasma byproduct mass recovery determination from recipe 1. Mass recoveries of 95% and 96% were obtained for the microwave power settings of 1000 and 1950 W, respectively. Shown in eq 5 is the balanced chemical reaction for the 1950 W plasma study of recipe 1:

$$5CF_4 + 50CHF_3 + 60Ar + 60H_2 + 60O_2 \Rightarrow 15CO_2 + 33CO + 8COF_2 + 155HF \quad (5)$$

The hazardous byproducts including hydrogen fluoride, HF, and carbonyl fluoride, COF_2, were both easily water scrubbed from the gaseous exhausts that exited the roughing vacuum system. The possibility of observing compounds such as OF_2 and F_2 was pursued. However, no such species were detected, and if any such compounds existed, they would have reacted with the approximately 300 parts per million (ppm) of H_2O formed. Also, the absence of the $NO^+ = 30$ peak in Figure 4 verifies that the plasma abatement of these etch recipes in the presence of nitrogen does not yield oxides of nitrogen, i.e., NO_x. Therefore, if this technology were incorporated into an industrial process the greenhouse gas byproducts would include CO, CO_2, and H_2O.

The mechanisms responsible for the final product distributions are extremely complex and involve neutrals, ions, and radicals. Table 3 lists the some of the pertinent elementary processes (*3*, *8*, *9*, *18*, *19*), which are responsible for the final byproduct nonequilibrium distributions. Further investigation is needed before definitive conclusions can be made. However, we consider that the processes in Table 3 should receive initial consideration. Reactions 6−10 involve the additive gases and some of their plasma generated intermediates. Reactions 11−15 are involved in the dissociation of CHF_3 and CF_4. Reactions 16−29 involve plasma-generated intermediates that could be important in determining the final product distribution. However, the simplicity of the species produced by the plasma reaction (diatomic and triatomic molecules) gives some insight into the nonequilibrium and nonthermal nature of this plasma abatement

TABLE 3. Important Elementary Reactions

reactants		products	eq	reactants		products	eq
$H_2 + e^-$	⇒	$2H + e^-$	6	$CF_3 + H$	⇒	$CF_2 + HF$	18
$H + O_2$	⇒	$OH + O$	7	$CF + O_2$	⇒	$CO + OF$	19
$O + H_2$	⇒	$OH + H$	8	$CF_2 + e^-$	⇒	$CF + F + e^-$	20
$OH + H$	⇒	H_2O	9	$CF_2 + H$	⇒	$CF + HF$	21
$H + F$	⇒	HF	10	$OF + H_2O$	⇒	$HO_2 + HF$	22
$CHF_3 + e^-$	⇒	$CF_3 + H + e^-$	11	$CF + H_2O$	⇒	$CFH + OH$	23
$CHF_3 + e^-$	⇒	$CF_2 + HF + e^-$	12	$CFH + OH$	⇒	$CO + HF$	24
$CHF_3 + OH$	⇒	$CF_3 + H_2O$	13	$CF + H$	⇒	CFH	25
$CF_4 + e^-$	⇒	$CF_2 + F_2 + e^-$	14	$CFH + O$	⇒	$CO + HF$	26
$CF_4 + e^-$	⇒	$CF_3 + F$	15	$CF_2 + OH$	⇒	$HOCF_2$	27
$CF_3 + OH$	⇒	$COF_2 + HF$	16	$HOCF_2$	⇒	$COF + HF$	28
$COF_2 + H_2O$	⇒	$CO_2 + 2HF$	17	$COF + OH$	⇒	$CO_2^+ HF$	29

technique. Since the surface wave plasma medium is emitting photons, optical dissociation pathways may also play a role. A detailed theoretical study for the unimolecular reaction dissociation channels of CHF_3 validated that HF elimination is the dominant process for photon excitation at energies <7.0 eV (*20*). As for CF_4, it is expected that electron impact is the critical initial process in its destruction and an extensive review of electron interactions with CF_4 has been published (*9*). Below a threshold of 12.5 eV for electronic excitation, vibrational excitation is the dominant inelastic process. Vibrational excitation is dominated by the ν_3 and ν_4 infrared active modes via direct dipole scattering in the resonance region. Furthermore, all electronic excitations of CF_4 lead to dissociation. Above this 12.5-eV threshold the dissociation of CF_4 into neutrals begins and dominates until ionization sets in and progressively yields to dissociative ionization. This process then takes over and accounts, at sufficiently high impact energies (>35 eV), for the total electronic excitation cross section. Cross sections for positive ion pair formation, multiple ionization, and positive ion-negative ion pair formation are generally smaller than those for single ionization in the low energy range (<100 eV). The electron temperatures in surface wave plasmas are typically in the range of 5000−10000 K which corresponds to an average electron energy of 0.5−1.0 eV. Therefore, if the electron impact dissociation of CF_4 is the dominant initial rate-determining step, then we must conclude that the destruction processes must be dominated by elementary reactions involving inelastic vibrational excitation. Furthermore, unlike Inductively Coupled Plasma (ICP) processes, detailed studies on the fundamental properties of microwave plasmas (electron number density, temperatures, etc.) are scarce. Clearly, an in-depth investigation of the elementary processes occurring at the molecular level will be necessary for a fundamental understanding of this technology.

In conclusion, this study demonstrates the feasibility of utilizing microwave-generated surface wave plasmas to destroy and remove tetrafluoromethane and trifluoromethane emanating from semiconductor plasma etch tools. A substantial decrease in the GWP (100 ITH) of 6500:1 of the waste gases exiting these tools can be realized by plasma abatement of the unused PFCs. Furthermore, the chemical byproducts are all simple, low molecular weight compounds, and the fluorinated byproducts can be easily water scrubbed and neutralized. As expected in these oxygen-rich conditions, we did not observe any soot formation within the plasma tube that would hinder continuous operation. These aforementioned characteristics make surface wave discharges an attractive technology for the destruction and removal of thermally stable gases emanating from low-pressure industrial processes such as semiconductor fabrication tools.

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