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Some Chemical Aspects of the Fluorocarbon Plasma Etching of Silicon and Its Compounds

Mass spectrometric sampling of fluorocarbon glow discharges and in situ measurements of the etch rate of Si and SiO_2 with quartz crystal microbalances have been used to provide additional insight concerning the chemistry involved when additive gases such as O_2, H_2, N_2, H_2O, and C_2F_4 are injected into a CF_4 glow discharge. The results obtained in our low-pressure, long-residence-time system indicate that the etching behavior of the discharge is not significantly influenced by the molecular structure of the injected gas molecules but is determined primarily by the elemental composition of the glow discharge. This phenomenologically observed result can be used to predict qualitatively the relative etching behavior of a large class of gaseous etchant mixtures as well as the role of various electrode or wall materials in the plasma etching process. Although this oversimplified interpretation should not be extended to short-residence-time plasma systems, it is believed to be valid for some of the configurations used in plasma etching and reactive ion etching.

Introduction

It has been recognized by many workers [1-10] that the addition of chemically active gases such as oxygen and hydrogen to fluorocarbon plasma etching discharges usually results in significant and often selective changes in the etch rates of silicon, silicon dioxide, and other materials of interest in semiconductor device manufacture. These results are most often explained in terms of the creation or suppression of certain chemically active species in the gas phase by the additive gas [2, 4, 7]. It is important that a more complete understanding of the discharge chemistry be developed; in semiconductor device manufacture, there is a need for etch rate selectivity and that selectivity can be obtained by using certain additive gases [2, 8, 10].

In this study, evidence will be presented which indicates that the etching behavior of a fluorocarbon glow discharge, in certain experimental configurations, can be thought of in terms of the "effective" fluorine-to-carbon ratio of the injected gases.

Experimental procedure

The apparatus, shown in Figs. 1(a-b), is a slightly modified version of a previously described plasma diagnostic system [11, 12]. A glow discharge is established by capacitively applying a 13.56 MHz rf voltage to the water-cooled excitation electrode. In this work the pressure of the etching gas is typically in the range of 2-3 Pa (≈20 millitorr) and the gas flow, maintained by a liquid-nitrogen-trapped mechanical pump, is in the range of 2-3 Pa-liters/s (≈2 cm^3/min). The volume of the upper chamber, in which the glow discharge is established, is 92 liters but the volume of the discharge itself is only 1 to 2 liters. These conditions correspond to long residence times for species in the vacuum chamber (≈1 min) and in the plasma (≈1 s). The chambers containing the energy analyzer and the quadrupole mass spectrometers are pumped with a 15-cm oil diffusion pump that can maintain pressures in the 10^{-4} Pa (10^{-6} torr) range with the upper chamber at discharge pressure. The sampling orifice in the substrate plane is 0.8 mm in diameter, whereas the sampling orifice in the effluent gas stream is 0.2 mm in diameter.

In this work the discharge behavior is monitored by mass spectrometric measurements of the positive ions extracted directly from the glow discharge volume [11, 12] and by mass spectrometric analysis of neutral species in

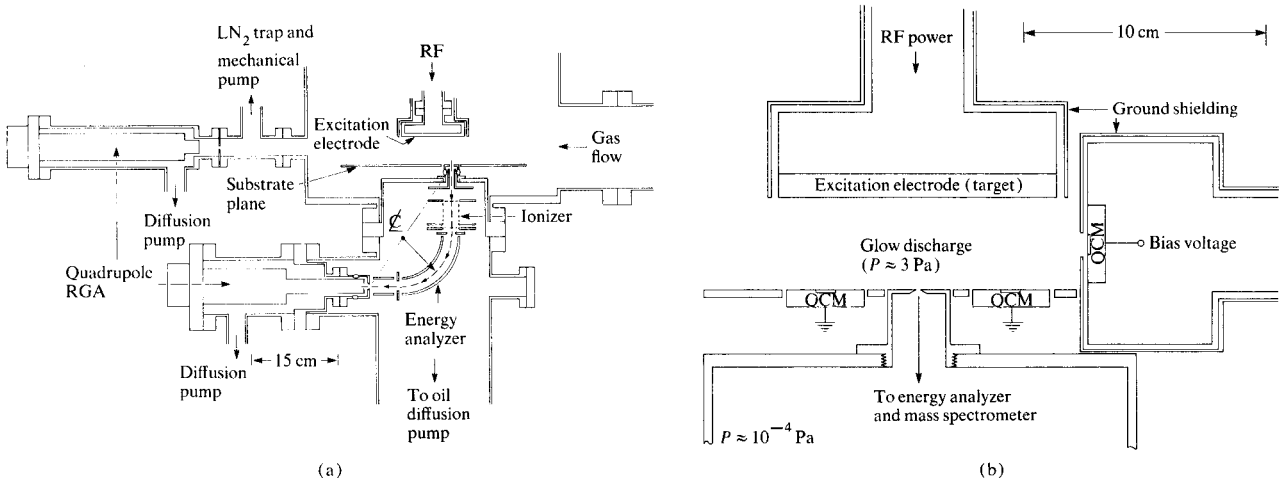

Figure 1 (a) Schematic diagram of experimental system. (b) Schematic diagram of the discharge region showing the locations of the quartz crystal microbalances.

Table 1 Silicon etching and polymerization behavior of various etch gases. The plasma potential in this work was about 20 V and the wafers were grounded in the no-ion-bombardment case. The wafers were biased at −200 V to study the effects of ion bombardment using the microbalance located at the side of the discharge as shown in Fig. 1(b). Discharge conditions: SiO_2 excitation electrode area 100 cm^2; 13.56 MHz rf power ≈ 100 W; interelectrode spacing, 4 cm; pressure ≈ 2.5 Pa; gas flow ≈ 2 Pa-liters/s.

Gas	*F/C ratio*	*No ion bombardment*	*Ion bombardment*
CF_4	4	etch	etch
C_2F_6	3	≈ 0	etch
C_3F_8	2.67	polymerize	etch
i-C_4F_{10}	2.5	polymerize	etch
C_2F_4	2.0	polymerize	polymerize
CHF_3	3–2	polymerize	etch
CH_2F_2	2–0	polymerize	polymerize

the effluent gas. The positive ion analysis is carried out by the quadrupole mass filter following the energy analyzer as shown in Fig. 1(a). The effluent gas analysis is performed by a second quadrupole mass filter, shown in the upper left of Fig. 1(a). These mass spectrometric measurements are supplemented with *in situ* measurements of the etch rate of both Si and SiO_2, accomplished by using two quartz crystal microbalances located in the grounded plane adjacent to the sampling orifice, as shown in Fig. 1(b). [These microbalances are not shown in Fig. 1(a) in order to simplify the figure.] The Si and SiO_2 thin films were deposited onto the microbalances by thermal vaporization prior to their installation in the discharge chamber. Normally, when this planar-diode low-pressure approach is used in plasma etching, the wafers to be etched are placed on the negatively biased excitation electrode (reactive ion etching or reactive sputter etching [5, 10, 13, 14]), and it is recognized that ion bombardment can play a major role in the etching process. In order to include the effects of ion bombardment in this study, a third microbalance was installed in the system, as shown in Fig. 1(b). A negative potential could be applied to this microbalance so that the effects of positive ion bombardment on the etching chemistry could be studied. The microbalance had a small enough area (0.7 cm^2) that it was possible to apply negative potentials of several hundred volts to the microbalance without significantly influencing the nature of the discharge.

In most of this work the excitation electrode was SiO_2 (100 cm^2 area). The nature of the excitation electrode has a large effect on the discharge chemistry in this low-gas-flow system [11], and in those cases where the oxygen generated by the etching of the SiO_2 excitation electrode obscures or interferes with the phenomena of interest, other electrode materials have been used. These instances are emphasized in the text and a short discussion of electrode effects is given in the next section.

Results

Pure fluorocarbon etch gases

The etching characteristics of the following fluorocarbon etch gases have been studied: CF_4, C_2F_6, C_3F_8, i-C_4F_{10},

and CF_4-C_2F_4 mixtures. The etching behavior of Si in our system with these gases is described qualitatively in the upper portion of Table 1. These results pertain to the long-residence-time, low-pressure type of glow discharge used in this study. When shorter residence times and higher pressures were used, etching was observed on grounded Si surfaces with both C_2F_6 and C_3F_8 etch gases, as has been reported elsewhere [2]. The situation is further complicated by the fact that it is sometimes difficult to determine the extent of the positive ion bombardment on a grounded or floating surface in a specific plasma system because of uncertainties concerning the plasma potential [15]. Also, the partial pressure of background gases, unless very low, can be expected to influence the discharge chemistry. However, the observation that ion bombardment suppresses polymerization and promotes etching for fluorine/carbon (F/C) ratios greater than about two can be expected to apply generally. The mechanism by which the onset of polymerization is retarded by ion bombardment is probably similar to the "ion-assisted etching" process that has been described elsewhere [10, 16], in which the probability that gas phase F atoms react with a surface is increased when that surface is subjected to ion bombardment. Physical sputtering may also play a role in preventing polymerization at higher ion energies. When unsaturated monomers such as C_2F_4 are used, ion bombardment of a surface does not lead to etching but, in fact, enhances the rate of polymerization. The reason for these seemingly contradictory effects of ion bombardment is believed to result, in the case of saturated monomers, from the rate-limiting step in the polymerization process being the generation of unsaturated gas phase species that can bond to surface radical sites. When unsaturated monomers are used, the monomer itself can bond to surface radical sites and the rate-limiting step now involves the generation of these sites on the surface. Ion bombardment will increase the rate of generation of surface radical sites, thus increasing the polymerization rate when unsaturated monomers are used.

We feel it is inappropriate to compare quantitatively the etch rates of various gases used in this study, not only because these rates are inevitably highly system dependent, but also because of uncertainties as to what parameters should be kept constant in such a comparison (i.e., molecular flow, molecular pressure, F atom or C atom flow or pressure, etc.).

Heinecke [2] first reported the observation that the etch rate of Si decreased relative to the etch rate of SiO_2 as the etch gas was made fluorine deficient with respect to CF_4. In the present work the influence of decreasing the fluorine-to-carbon (F/C) ratio was studied by adding C_2F_4 to a CF_4 discharge, and by measuring the etch rates of Si and SiO_2 simultaneously. The results are shown in Fig 2(a). Several points should be emphasized:

a. The etch-rate ratio of SiO_2 to Si increases as the F/C ratio is decreased (in this case by adding C_2F_4 to CF_4).
b. The low etch rates in Fig. 2(a) are a result of using low rf power, low gas-flow rates, and low pressures. Low etch rates were used so that the entire run could be completed before the 2-μm-thick films on the microbalances were consumed. Similar qualitative effects are to be expected at higher etch rates.
c. Polymerization begins to take place when the etch-gas composition is about 1:1 CF_4 to C_2F_4. This is the same elemental composition as C_3F_8, and recall from Table 1 that C_3F_8 discharges also caused polymerization on grounded surfaces; i.e., the etching behavior of a CF_4-C_2F_4 (1:1) discharge appears similar to that of a C_3F_8 discharge.

Table 2 Mass spectral data for positive ions extracted from glow discharges of C_3F_8 and CF_4:C_2F_4 (1:1). Discharge conditions as in Table 1. The SiO_2 excitation electrode is the source of oxygen in these spectra, whereas the hydrogen is a contaminant in the vacuum system.

Mass no.	*Ion*	*Relative peak intensities*	
		C_3F_8	CF_4:C_2F_4 *(1:1)*
28	CO^+	0.9	3.5
31	CF^+	3.2	4.6
47	COF^+	3.3	10
50	CF_2^+	1.3	2.2
51	CF_2H^+	6.5	23
66	COF_2^+	0.4	3.7
69	CF_3^+	100	100
85	SiF_3^+	1.5	2.1
93	$C_3F_3^+$	2.8	0.3
100	$C_2F_4^+$	13.5	2.0
119	$C_2F_5^+$	12.6	3.7
131	$C_3F_5^+$	14.1	0.6
150	$C_3F_6^+$	2.1	0.1
169	$C_3F_7^+$	7.4	0.6
181	$C_4F_7^+$	4.6	0.5

The major peaks in the mass spectra of the positive ions extracted from C_3F_8 and CF_4-C_2F_4 (1:1) discharges are shown in Table 2. In both cases the CF_3^+ peak dominates, and although the relative intensities of the peaks vary significantly, the peak distributions are similar in the sense that any peak with an intensity greater than about two percent of the CF_3^+ peak in either spectrum is present in

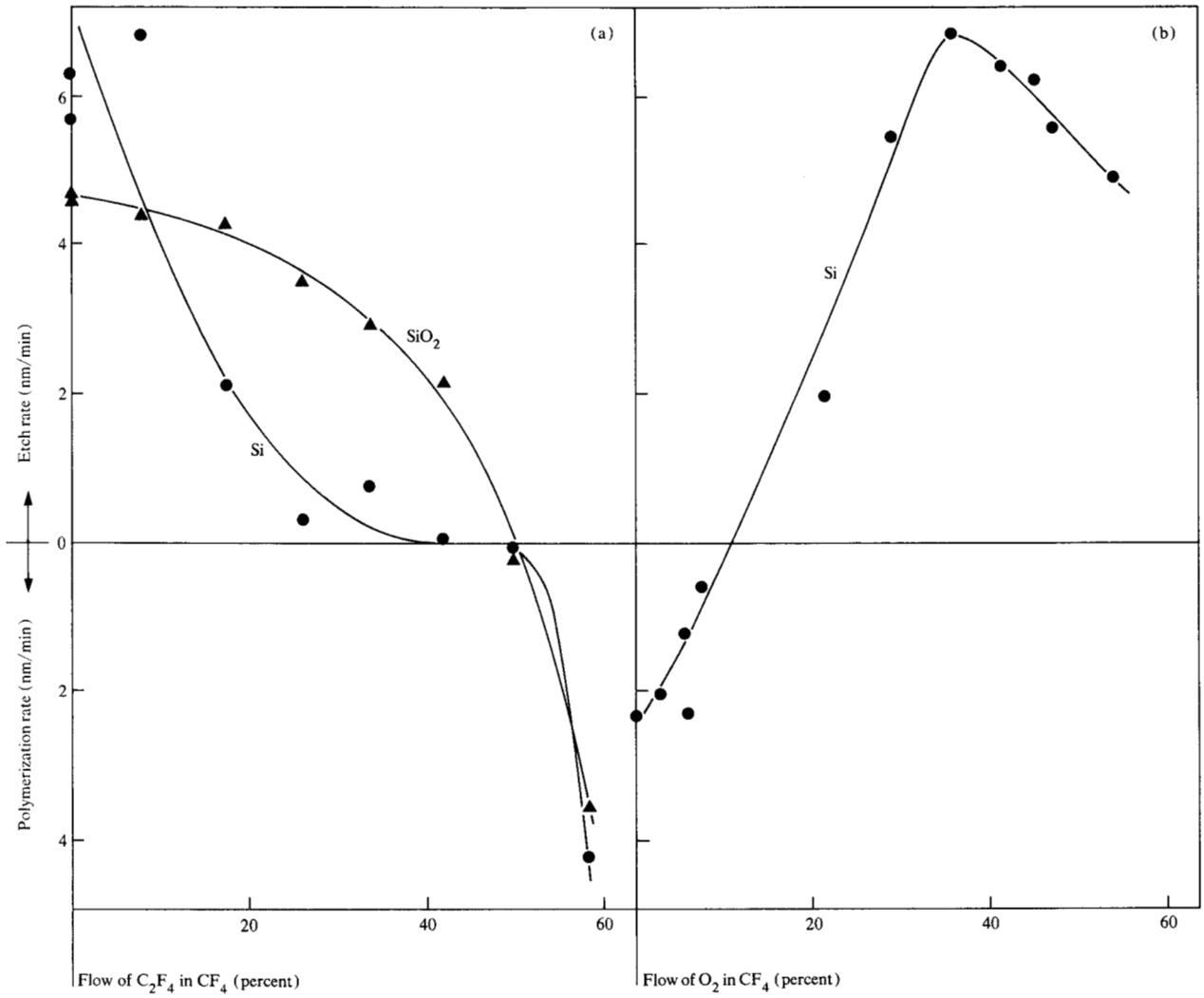

Figure 2 (a) Etch rates of Si and SiO_2 as a function of the percentage by flow rate (molecules/s) of C_2F_4 in CF_4. (SiO_2 excitation electrode area of 100 cm^2, 13.56 MHz rf power ≈ 100 W, interelectrode spacing of 4 cm, pressure ≈ 3 Pa, total gas flow ≈ 2 Pa-liter/s). (b) Si etch rate as a function of the percentage by flow rate (molecules/s) of oxygen in CF_4. (Si excitation electrode area of 100 cm^2, 13.56 MHz rf power ≈ 100 W, interelectrode spacing of 4 cm, pressure 3 to 4 Pa, CF_4 gas flow ≈ 2 Pa-liter/s.)

both spectra. It should be emphasized that the relative intensities of the peaks in these spectra do not necessarily reflect the density of the neutral species because of both inevitable fragmentation of molecular species during ionization, and ion-molecule reactions that can selectively distort the density of various ionic species.

Conventional electron-impact-ionization mass spectrometry of the effluent gas showed that the C_2F_4 concentration was of the order of one or two percent of the CF_4 concentration when the gas composition injected into the glow discharge was 1:1.3 (CF_4 to C_2F_4). Two reasons for the dominance of CF_4 relative to C_2F_4 in the effluent gas can be suggested:

a. The C_2F_4 can be expected to chemisorb on various surfaces in the vacuum system and the chemisorption may be dissociative. If the chemisorption is not dissociative, the flux of energetic species (electrons, ions) incident on these surfaces will probably dissociate the chemisorbed molecule. Therefore, there exists a dissociation mechanism for C_2F_4 which does not apply to CF_4 because CF_4 does not chemisorb on surfaces [17].
b. It is suspected that, in the absence of significant quantities of oxygen, recombination processes consume a substantial fraction of the fluorocarbon and fluorine radicals [17]. An example of such a recombination process is $\cdot CF_3 + \cdot F \rightarrow CF_4$, and one would expect CF_4

to be the species most often formed by recombination. Thus, there exists a process which can result in the generation of significant amounts of CF_4, whereas one would not expect large amounts of C_2F_4 to be formed by recombination of radicals. It is not clear which of the two mechanisms leads to the low concentration of C_2F_4 relative to CF_4 in the effluent gas.

Oxygen added to fluorocarbon etch gases

Many workers [1, 3-7, 9, 10] have recognized that the addition of molecular oxygen to fluorocarbon plasma etching discharges usually results in a significant increase in the etch rate of Si. In the work to be described below, the chemical effects of oxygen have been studied in the following systems:

a. $CF_4 + O_2$
b. Oxygen-containing fluorocarbon monomers such as carbonyl difluoride (F_2CO), bis(trifluoromethyl)-peroxide (F_3COOCF_3), trifluoroacetic anhydride [$(F_3CCO)_2O$], and hexafluoroacetone [$(F_3C)_2CO$]
c. $C_2F_4 + O_2$
d. Pure O_2, with a polytetrafluoroethylene (PTFE) excitation electrode

In order to study the effects of adding oxygen to CF_4 it was necessary to replace the SiO_2 excitation electrode with Si (to eliminate the oxygen liberated by the etching of the SiO_2 electrode). When an electrode such as Si is used in our low-flow-rate system, enough fluorine is consumed by the etching of the electrode material to cause significant unsaturation in the gas phase. This in turn leads to polymer formation on grounded surfaces and has been discussed previously [11]. The addition of oxygen to the system causes a change from polymerization to etching, as is shown in Fig. 2(b). In terms of the F/C ratio discussed in the previous section, oxygen can be considered to increase the F/C ratio if, in the determination of this ratio, we include only active etching species. That is, stable molecules such as CO and CO_2, which are not expected to participate in polymerization or etching, are not included in the F/C ratio. Consequently, oxygen can be thought of as a carbon scavenger.

As might be expected, oxygen-containing fluorocarbon molecules can also be used for plasma etching. Some qualitative results obtained by using four such etching gases are given in Table 3. In this table the oxygen-to-carbon (O/C) ratio has been used to characterize the chemical composition of the gas instead of the F/C ratio used in Table 1. The reason for this choice is that when carbon is bonded to oxygen and fluorine in a molecule, dissociation usually creates fluorine atoms. However, if there is no C—O bonding present, trifluoromethyl radicals ($F_3C\cdot$) are often formed more readily than fluorine atoms. For example, both F_2CO and $(CF_3)_2CO$ have a F/C ratio of 2, but F_2CO is a much better source of fluorine atoms and therefore etches Si more rapidly.

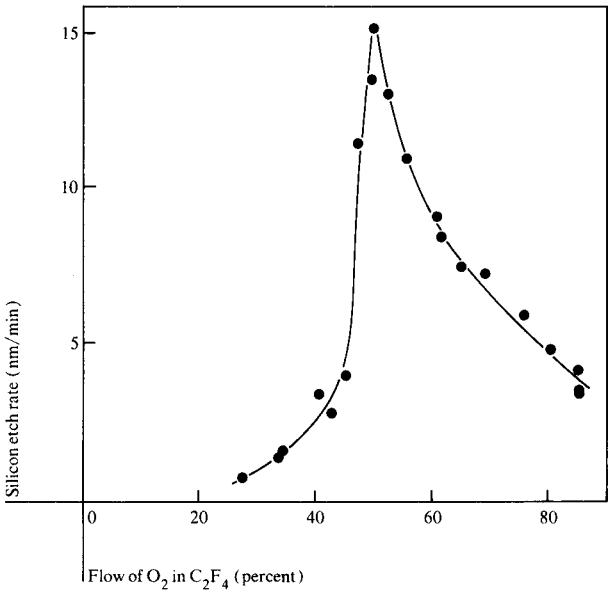

Figure 3 Silicon etch rate as a function of the percentage by flow rate (molecules/s) of oxygen in C_2F_4. (SiO_2 excitation electrode area of 100 cm^2, 13.56 MHz rf power ≈ 50 W, interelectrode spacing of 4 cm, pressure 5 to 10 Pa, C_2F_4 gas flow ≈ 3.7 Pa-liter/s.)

Table 3 Oxygen-containing fluorocarbon monomers used to plasma etch silicon. (Discharge conditions as in Table 1.)

Etching gas	*O/C ratio*	*Si etch rate (no ion bombardment)*
carbonyl difluoride, F_2CO	1	fast
bis(trifluoromethyl)peroxide, $(CF_3)_2O_2$	1	fast
trifluoroacetic anhydride, $(CF_3CO)_2O$	0.75	medium
hexafluoroacetone, $(CF_3)_2CO$	0.33	slow

Unsaturated monomers inevitably lead to polymerization upon exposure to a glow discharge, but in a manner similar to that shown in Fig. 2(b), glow discharges of unsaturated fluorocarbon monomers can be converted to etching discharges by the addition of oxygen. In Fig. 3 the etch rate of silicon is plotted vs the percentage of oxygen in a C_2F_4 discharge. Since the total gas flow was kept constant in this measurement, the decrease in the etch rate for high oxygen partial pressures is due largely to there

Table 4 Mass spectral data for effluent gas from plasma etching system for three etch gases. Discharge conditions are as in Table 1; PTFE electrode was used with the oxygen discharge.

Mass no.	*Ion*	*Relative peak intensities*		
		F_2CO discharge	*C_2F_4-O_2 (1:1) discharge*	*O_2 discharge PTFE electrode*
12	C^+	9.6	25	15
16	O^+	7.8	25	18
17	OH^+	2.1	0.4	3.5
18	H_2O^+	9.8	6.5	16
19	F^+	3.5	4.6	3.1
20	HF^+	25	21	26
28	CO^+	100	100	100
31	CF^+	4.6	10	6.5
32	O_2^+	7.9	30	21
38	F_2^+	0.3	—	—
44	CO_2^+	46	54	42
47	COF^+	46	39	30
50	CF_2^+	3.2	5.3	5.9
66	COF_2^+	25	8.7	8.1
69	CF_3^+	18	36	69
85	SiF_3^+	5.9	4.3	[a]

[a]The SiF_3^+ arises from the etching of the SiO_2 excitation electrode used with the F_2CO and C_2F_4-O_2 (1:1) discharges.

being less C_2F_4 (and therefore less fluorine available) as the oxygen percentage becomes large. If one corrects for this by plotting the etching efficiency per C_2F_4 molecule [i.e., by multiplying the etch rate in Fig. 3 by $100/(100 - X)$ where X is the O_2 percentage], one finds that the etching efficiency is relatively constant for large O_2 concentrations.

The influence of oxygen on the etching chemistry can be shown in yet another way, by using a pure oxygen discharge with a polytetrafluoroethylene (PTFE) excitation electrode. A significant Si etch rate (at the grounded Si-coated microbalance) was obtained in this way, where presumably oxygen is combining with carbon in PTFE, liberating fluorine that can etch Si.

Three of the systems discussed above can be used to provide what is probably our best evidence for the insignificance of chemical structure in our plasma environment. Whereas F_2CO, C_2F_4-O_2 (1:1), and O_2 (PTFE excitation electrode) are three very different ways of generating carbon-oxygen-fluorine glow discharges, the etch rates of Si measured in these systems are quite similar, provided other parameters such as total pressure, flow rate, and rf power are kept constant. However, the most striking similarity in these three very different chemical systems is the mass spectra of the effluent gas (major peaks shown in Table 4). (It should be emphasized that these spectra were obtained on the effluent gas by using the downstream quadrupole mass filter and its electron-impact-ionization capability. The peaks listed in Table 2 are for positive ions extracted directly from the glow discharge.) The fact that the etching behavior and the effluent gas composition are so similar for three very different chemical systems is good evidence that, in this discharge configuration, the chemistry is determined primarily by the elemental composition of the gas phase species present in the plasma. This conclusion should not be extended to high-flow-rate plasma chemistry systems where it is known [18] that chemical structure is a dominant factor in determining discharge chemistry, but it may be valid in some of the low-flow-rate systems used for plasma etching in the reactive ion etching mode [5, 13].

As can be inferred from Table 4, the C_2F_4 is almost totally dissociated when the discharge is established in a C_2F_4-O_2 (1:1) mixture. The presence of C_2F_4 is indicated by both $C_2F_4^+$ and $C_2F_3^+$, and these peaks constitute a major part of the effluent gas mass spectra when the glow discharge is off. However, when the discharge is turned on, these peaks decrease rapidly until they are no longer observable, indicating almost complete dissociation of the C_2F_4 molecular species. As was discussed in the preceding section, chemisorption of the C_2F_4 on surfaces in the vacuum system may contribute to the dissociation of C_2F_4. In addition, it is known that oxygen atoms react with C_2F_4 molecules [19–21], and also that electronically excited C_2F_4 molecules react with oxygen molecules [20]. Therefore, in C_2F_4-O_2 discharges these reactions could contribute to the dissociation of C_2F_4.

Another point of interest in Table 4 is the presence of a significant CF_3^+ peak, presumably indicative of CF_4 in the effluent gas. Since it is very unlikely that CF_4 is created as a direct product of the dissociation of C_2F_4, the most logical source of the CF_4 is radical recombination. The fact that CF_4 is seen even in the presence of oxygen (oxygen will scavenge fluorocarbon radicals, and thus suppress recombination) can be taken as evidence that, in the absence of oxygen, recombination of radicals to form CF_4 will consume a significant fraction of the active species in plasma etching discharges. This concept was discussed in the preceding section and has been considered elsewhere [17].

The role of oxygen in fluorocarbon glow discharges is to combine with carbon to form CO, CO_2 or F_2CO. This has the effect of increasing the effective F/C ratio of the discharge because carbon is being converted to volatile species that are much less likely to play a role in etching

or polymerization reactions, compared to pure fluorocarbon species. There are several ways in which the oxidation of carbon can be accomplished:

a. Oxidation of elemental carbon from surfaces in the vacuum system. If the surfaces in the discharge can be kept free of carbon, the surfaces are more likely to be nonreactive to F atoms and other fluorocarbon radicals. Consequently recombination processes are suppressed [17] and more F is available for etching.
b. Oxidation of fluorocarbon polymers from surfaces in the vacuum system. Figures 2(b) and 3 and the fact that etching can be accomplished in a pure oxygen discharge with a PTFE excitation electrode demonstrate this effect. The oxidation of the carbon in the fluoropolymer leaves the fluorine available for etching.
c. Gas phase reactions between oxygen and the fluorocarbon molecular gas. It is suspected that this type of chemistry is significant in C_2F_4-O_2 discharges and can be expected to be important when any unsaturated fluorocarbon is used with oxygen. A similar type of gas phase chemistry has been invoked to explain the effect of oxygen on Si etch rates in CF_4 discharges [4, 7]. However, the fact that oxygen atoms are relatively unreactive toward CF_4 [7, 22] leads us to believe that this is not a major process in CF_4-O_2 discharges.
d. Reactions between oxygen and fluorocarbon radicals. Fluorocarbon radicals will react with oxygen to form F_2CO or CO. This reaction in itself both liberates F atoms for etching and decreases the rate at which these radicals recombine with themselves or with F atoms to form such unreactive species as CF_4 or C_2F_6. This latter radical-radical recombination process constitutes a loss mechanism for active fluorine.

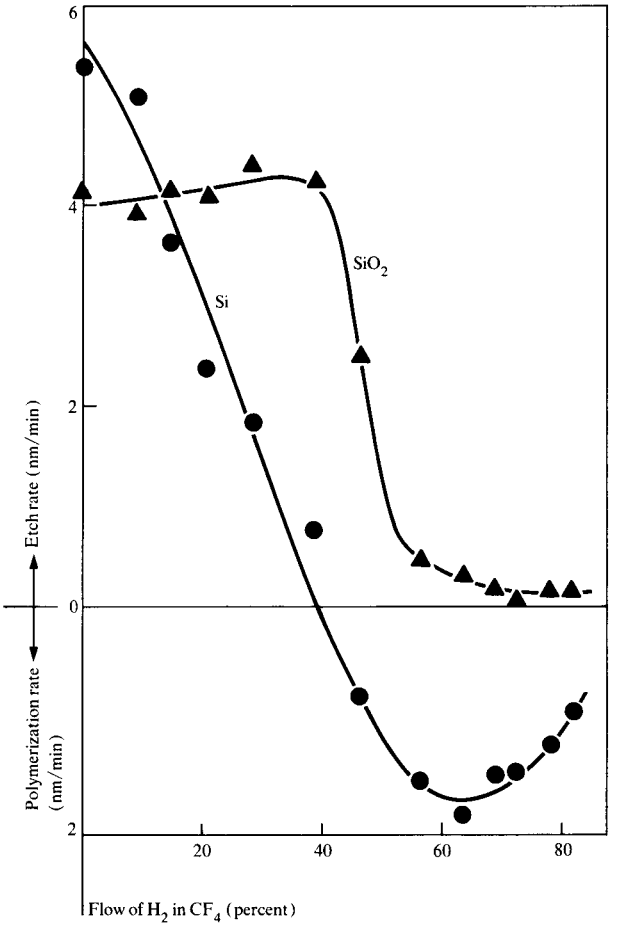

Figure 4 Etch rates of Si and SiO_2 as a function of the percentage by flow rate (molecules/s) of hydrogen in CF_4. (SiO_2 excitation electrode area of 100 cm^2, 13.56 MHz rf power ≈ 100 W, interelectrode spacing of 4 cm, pressure 3 to 5 Pa, CF_4 gas flow ≈ 2 Pa-liter/s.)

Hydrogen added to fluorocarbon etch gases

Heinecke [2] showed that the addition of hydrogen to fluorocarbon etch gases (either by adding H_2 to CF_4 or by using CHF_3) resulted in an increase in the etch rate ratio of SiO_2 with respect to Si. Ephrath [8] has optimized this technique in the reactive ion etching mode and has obtained SiO_2/Si etch rate ratios as high as 30.

In the present investigation the effect of hydrogen has been observed both by using CHF_3 and CH_2F_2 (see bottom of Table 1) and by adding H_2 to CF_4 (see Fig. 4). The main function of hydrogen is to scavenge fluorine by forming HF, which, as a diatomic molecule, is not likely to participate significantly in etching or polymerization chemistry. Consequently, fluorine in the form of HF is excluded from the effective F/C ratio and the addition of hydrogen to a fluorocarbon plasma will decrease this F/C ratio. In Table 1 the F/C ratio for CHF_3 and CH_2F_2 has included the possible fluorine scavenging role of hydrogen. If hydrogen does not scavenge fluorine the F/C ratio for CHF_3 is 3; whereas if hydrogen is 100 percent efficient in scavenging fluorine the effective F/C ratio is 2. With this concept in mind, it can be seen that the behavior of the partially fluorinated methanes is consistent with the behavior of the fluorocarbons at the top of Table 1.

The influence of adding H_2 to a CF_4 discharge on the etch rates of Si and SiO_2 (no ion bombardment) is shown in Fig. 4. As has been reported by others [2, 8], the etch rate ratio of SiO_2 to Si increases dramatically as H_2 is added to CF_4. Polymer formation occurs rather rapidly on Si (i.e., the Si-coated microbalance) whereas no polymer formation is observed on SiO_2. This measurement was repeated, with the positions of the Si and SiO_2 surfaces interchanged, to check for the possibility of this observation being caused by a geometrical asymmetry, but essen-

tially identical results were obtained. Either the condensation coefficient for the species responsible for polymer formation is very small in SiO_2 or the oxygen liberated by the very slight etching of SiO_2 is adequate to prevent the onset of polymerization.

Mass spectra of the effluent gas support the contention that the primary role of hydrogen is scavenging fluorine to form HF; the major hydrogen-containing peaks in the spectra were H_2 and HF. However, the mass spectra of the positive ions extracted from the discharge were rich in hydrogen-containing species. These ions are formed by various proton transfer reactions well known in chemical ionization mass spectrometry [23] and are not indicative of the relative concentrations of neutral species.

Nitrogen added to fluorocarbon etch gases

Whereas molecular nitrogen is not expected to influence fluorocarbon plasma-chemical behavior, atomic nitrogen created in the discharge could chemically combine with either carbon or fluorine. In order to search for chemical effects of adding N_2 to CF_4 discharges, as in the case of oxygen, a Si excitation electrode was used so that no oxygen was evolved from the excitation electrode. Recall that with a Si electrode in a low-pressure CF_4 discharge, polymerization was observed on grounded surfaces. As N_2 was added to the CF_4 discharge, the polymerization rate increased substantially for low N_2 concentrations and then slowly decreased as more N_2 was added. However, even with 40 percent N_2 (by flow) in the CF_4, polymerization was still observed on the grounded quartz crystal monitors, whereas only a small amount of O_2 was needed to suppress polymerization [Fig. 2(b)]. Consequently, as was concluded in a previous study [11], nitrogen is much less effective than oxygen in combining with carbon in a glow discharge environment. Mass spectra of the effluent gas revealed no indication of CN-containing compounds. However, the mass spectra of positive ions extracted from the discharge showed several large mass peaks that are assigned to ionic complexes involving the CN radical. These complexes [11] (e.g., $CF_4 \cdot CN^+$) are created by ion-molecule reactions and are not indicative of the concentration of neutral species. It appears as though N_2 plays a very minor chemical role (in the context of etching and polymerization) in fluorocarbon plasmas and can be thought of as essentially a diluent gas.

Other gases added to fluorocarbon etch gases

It has been shown that oxygen tends to increase the F/C ratio, that hydrogen decreases the F/C ratio, and that nitrogen has very little effect. With this information one can make informed guesses as to the effects of many other additive gases if the plasma conditions are such that the gases are efficiently dissociated in the discharge. For example, it is clear that adding hydrocarbons such as methane, ethane, ethylene, etc., decreases the effective F/C ratio, whereas adding oxides of nitrogen can be expected to increase the effective F/C ratio. In the case of water vapor, one has the competitive effects of oxygen and hydrogen. The net result is not easily predicted but it has been reported [6] that water vapor decreases the etch rate of Si and therefore decreases the F/C ratio. Water vapor has been used in the present study and our results indicate that water vapor does indeed decrease the effective F/C ratio. In fact, quite large SiO_2-to-Si etch rate ratios were obtained on grounded surfaces.

Electrode effects

It has been noted in this paper and elsewhere [11] that in this low-flow, low-pressure system, the nature of the excitation electrode significantly influences the discharge chemistry (i.e., the effective F/C ratio). For example, in a pure CF_4 discharge, etching is observed on grounded surfaces with a SiO_2 electrode, whereas polymerization occurs when a Si electrode is used. That is, the etching of the Si electrode has consumed fluorine and leads to unsaturation in the gas phase (i.e., a lower F/C ratio), whereas the oxygen liberated in the etching of the SiO_2 increases the F/C ratio and thus compensates the fluorine consumption of the Si component of SiO_2.

The chemical effects of a certain electrode material can be predicted with reasonable accuracy by considering the chemistry of the individual elements contained in the electrode. These effects are also very much dependent upon the volatility of the fluorides of the particular elements involved. If any element in an electrode forms an involatile fluoride (e.g., Al), the evolution of this material from the electrode will be determined by physical sputtering and, since physical sputtering rates are much lower than plasma etching rates that involve volatile compounds, the chemical effects will be small. Electrodes consisting of elements that form nonvolatile fluorides should be avoided in most situations because inevitably some of the involatile material sputtered from the electrode will arrive at the surface being etched; this can be a source of roughness [24] on the etched surface.

Most electrode materials tend to consume fluorine and thus decrease the F/C ratio. In addition to the Si example given in this paper, Mo, W, B, C, SiC, polyethylene $(CH_2)_n$, and polytetrafluoroethylene $(CF_2)_n$ are examples of readily available electrode materials that can significantly decrease the F/C ratio. Polytetrafluoroethylene itself has an F/C ratio of 2: thus, a PTFE electrode will only decrease the F/C ratio of the discharge if the F/C ratio in the gas phase is greater than 2 (always the case in plasma etching, as shown in Table 1).

Since oxygen is the species that best prevents carbon from participating in the plasma chemistry, if one wishes to use an electrode that increases the effective F/C ratio, one needs to maximize the oxygen per molecular unit of the electrode material ratio, while minimizing the number of fluorine-consuming atoms. As far as readily available materials are concerned, oxides of elements forming volatile fluorides (e.g., SiO_2, Ta_2O_5, etc.) appear to be the most successful. It should be noted that the amount of material evolved from an electrode in which there are no nonvolatile compounds formed can be a significant fraction of the etching gas flow if low gas flows ($\lesssim$20 cm^3/min) are used.

Summary

The plasma chemistry resulting from the addition of various additive gases to fluorocarbon (primarily CF_4) discharges has been examined by monitoring the etching characteristics of Si and SiO_2 and by mass spectrometry (observing the positive ions and neutral species in the discharge gas). The elemental composition of the discharge, represented by an effective F/C ratio, is used to characterize the discharge behavior. Hydrogen tends to cause unsaturation in the discharge (decreasing the F/C ratio), oxygen increases the F/C ratio, and nitrogen has very little chemical effect. Most electrode materials tend to decrease the F/C ratio.

In order to obtain high SiO_2-to-Si etch rate ratios, it is necessary to decrease the F/C ratio of the discharge. The mechanism [11, 16] that is believed to be responsible for the preferential decrease of the Si etch rate is based on achieving a balance between the carbon and fluorine chemisorption on Si, such that most of the arriving fluorine is required to volatilize the carbon as CF_4, and little if any is left over to form SiF_4. However, on SiO_2 the oxygen in the lattice is able to volatilize the carbon as CO, CO_2, or F_2CO, and most of the fluorine is still available to form SiF_4.

The general theme which pervades this discussion is that, in the long-residence-time, low-pressure glow discharges used in this work, the chemistry occurring in the plasma is determined primarily by the elemental composition of the discharge species and not by the molecular nature of the gases used. This is certainly not true in high-flow-rate systems but may be applicable to some of the lower-flow-rate systems used for reactive ion etching.

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