Plasma–surface interactions in fluorocarbon etching of silicon dioxide

J. W. Butterbaugh, D. C. Gray, and H. H. Sawin

Articles you may be interested in

Role of steady state fluorocarbon films in the etching of silicon dioxide using CHF_3 in an inductively coupled plasma reactor
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **15**, 1881 (1997); 10.1116/1.580655

Study of the SiO_2-to-Si_3N_4 etch selectivity mechanism in inductively coupled fluorocarbon plasmas and a comparison with the SiO_2-to-Si mechanism
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **17**, 26 (1999); 10.1116/1.582108

Plasma etching of Si and SiO_2—The effect of oxygen additions to CF_4 plasmas
Journal of Applied Physics **49**, 3796 (1978); 10.1063/1.325382

Fluorocarbon high-density plasmas. II. Silicon dioxide and silicon etching using CF_4 and CHF_3
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **12**, 333 (1994); 10.1116/1.578877

Fluorocarbon high-density plasmas. I. Fluorocarbon film deposition and etching using CF_4 and CHF_3
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **12**, 323 (1994); 10.1116/1.578876

High density fluorocarbon etching of silicon in an inductively coupled plasma: Mechanism of etching through a thick steady state fluorocarbon layer
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **16**, 239 (1998); 10.1116/1.580978

Plasma–surface interactions in fluorocarbon etching of silicon dioxide

J. W. Butterbaugh

IBM General Technology Division, Essex Junction, Vermont 05452

D. C. Gray and H. H. Sawin

Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, Massachusetts 02139

The major species present in a fluorocarbon plasma environment were simulated and independently controlled using radical and ion beams in an ultrahigh-vacuum apparatus. The beams used in this study were chosen to determine the importance of CF_x radicals in a CF_4 plasma; the beams included F and CF_2, with a beam of Ar^+ to simulate energetic ion bombardment. Both CF_2 and F enhance the etching yield of SiO_2 under energetic Ar^+ bombardment; however, the enhancement with F is twice that seen with CF_2 at similar fluxes. When CF_2 and F fluxes are used simultaneously, F dominates and the CF_2 flux has little effect on the overall etching yield. Combined with previous work on Si substrates, these results are consistent with qualitative theories for SiO_2/Si selectivity in fluorocarbon plasmas. Possible elementary steps in the ion-enhanced etching process are proposed and reduced to a two-parameter model which represents the process as ion-enhanced neutral adsorption followed by ion-induced reaction to form volatile products.

I. INTRODUCTION

During plasma-etching processes, the substrate surface is subjected to fluxes of several different reactive species. In fluorocarbon plasmas, the species striking the substrate surface include CF_y ($y = 0$–3), F, and energetic CF_x^+ ($x = 0$–3). Knowledge of the relative importance of these species in the plasma etching of SiO_2 is necessary to understand selectivity and anisotropy in SiO_2 etching processes. Selectivity of SiO_2 etching over Si etching in fluorocarbon plasmas is attributed to carbonaceous film formation on the Si surface, while the highly anisotropic nature of SiO_2 etching is attributed to the strongly ion-enhanced nature of the etching process. Previous research into these mechanisms has included post-process surface analysis with x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and ellipsometry. Other research efforts have focused on the relative importance of the radical and ionic species by isolating these species outside the plasma environment.

The general conclusion of the post-process surface studies is that a carbonaceous film forms on the surface of Si while little, if any, carbonaceous film forms on the surface of SiO_2. After exposing Si and SiO_2 surfaces to a C_2F_6 plasma, Oshima[1] found a 20- to 30-Å-thick fluorocarbon film on the Si surfaces and little or no fluorocarbon film on the SiO_2 surfaces. Coburn[2] found similar results with AES analysis of Si and SiO_2 surfaces after exposure to $CF_4 + H_2$ plasmas. Coburn found that the C signal on Si surfaces increases and the Si signal decreases as the amount of H_2 in the plasma is increased; the C signal is not detectable on SiO_2 surfaces until the level of H_2 addition is above 17%. Jaso and Oehrlein,[3] using XPS and ellipsometry, also noted the absence of any carbonaceous film on SiO_2 surfaces, although some Si–C bonding was detected. Haverlag et al.[4] studied the SiO_2 surface in a CF_4 plasma with *in situ* ellipsometry and again found a carbonaceous layer only on the Si after the SiO_2 was

etched away. The probable explanation for the absence of a carbon layer on the SiO_2 surface is the availability of oxygen to form volatile carbon-fluorine-oxygen species. *Ab initio* calculations[5] show COF_2 to be very weakly bound on SiO_2 surfaces, making it a likely product of the etching process.

Several studies in the literature have isolated radical species present in the discharge and have measured their reactivity towards SiO_2.[6,13] Flamm et al.[6] measured the reactivity of atomic fluorine with SiO_2 and found that F will spontaneously etch SiO_2 at a rate similar to that found in CF_4 barrel etchers, where the SiO_2 surface is subjected to little ion bombardment. Etching rates in parallel-plate or reactive ion etching (RIE) reactors, where the SiO_2 receives considerable energetic ion bombardment, are much higher than can be accounted for by spontaneous reaction with F.

The reactivity of CF_2 with SiO_2 has been studied by several researchers.[7–10] Selamoglu et al.[9] reported that SiO_2 does not etch in the presence of CF_2 without simultaneous surface irradiation. Langan et al.[10] performed XPS analysis of SiO_2 surfaces exposed to CF_2 radicals and found that CF_2 adsorbs on the SiO_2 surface, but does not dissociate or react with the surface. After bombarding the surface with energetic ions, the CF_2 adsorption probability increased, but there was still negligible dissociation. These studies clearly show that CF_2 does not spontaneously etch SiO_2; CF_2 will only etch SiO_2 when the surface is under simultaneous energy irradiation (e.g., ion bombardment).

The reactivity of CF_3 towards SiO_2 has also been studied by several researchers.[6,11–13] These studies reported that the reactivity of CF_3 toward SiO_2 is below experimental detection limits, placing the reaction probability at less than 10^{-6}. Joyce et al.[12] found that CF_3 will adsorb on SiO_2, but will undergo very limited dissociation. XPS analysis, after exposure to CF_3, showed no evidence of O–F bonding and some evidence of both C–Si and C–O bonding.[12] McFeely et al.[13] used XPS to examine SiO_2 surfaces exposed to CF_3 and

also determined that CF$_3$ adsorbs, but not dissociatively. In addition, McFeely concluded that adsorbed CF$_3$ is mainly bound to O on the surface through C–O bonding. These studies show that CF$_3$, like CF$_2$, does not spontaneously etch SiO$_2$.

In addition to the flux of neutral radical species, there is significant ion bombardment of the SiO$_2$ surface in a parallel-plate plasma reactor. Ions in a CF$_4$ plasma are mainly CF$_3^+$, CF$_2^+$, and CF$^+$. Several studies[14-18] demonstrate that these molecular ions, which supply chemical reactants to the surface as well as energy, remove a larger number of SiO$_2$ molecules than a noble gas ion like Ar$^+$. The etching yield (number of SiO$_2$ molecules removed per incoming ion) has been measured at 0.2 for 500 eV Ar$^+$ and 0.5 for 500 eV CF$_x^+$.[18] It has also been shown that the energetic ion bombardment can induce the reaction of species already adsorbed on the surface. The SiO$_2$ etching yield of Ar$^+$ is enhanced when the surface is simultaneously exposed to a neutral source of F, such as XeF$_2$.[15,19] Because XeF$_2$ dissociatively chemisorbs leaving a monolayer of F on the SiO$_2$ surface,[19] XeF$_2$ has been used to simulate the flux of atomic fluorine in the plasma environment. Loudiana et al.[19] found an enhancement of the 500 eV Ar$^+$ etching yield of about 3.6$\times$ with simultaneous XeF$_2$ exposure.

It has also been suggested that the etching yield of SiO$_2$ is enhanced by the adsorption of neutral CF$_y$ species. In studies using CF$_x^+$, the SiO$_2$ is also exposed to CF$_y$ species, which are produced along with the ions. Mayer and Barker[20] attributed the pressure dependence of the etching rate in reactive ion beam etching to the adsorption of neutral species. The pressure dependence flattened out at higher pressure, indicating a saturation or a shift from an adsorption-limited to an ion flux limited etching process.

In the present work, the fluxes to a SiO$_2$ surface in a fluorocarbon plasma environment are simulated with three controlled beams in an ultrahigh-vacuum (UHV) apparatus. In the literature, the primary etchant in a CF$_4$ plasma has been identified as atomic fluorine, although it has been suggested that CF$_2$ and CF$_3$ may be active participants in the etching reaction;[21,22] a beam of atomic fluorine (F) was used as the primary etchant in the UHV apparatus. There are several fluorocarbon radical species present in the CF$_4$ plasma, including CF$_3$, CF$_2$, and CF; a beam of CF$_2$ was used to represent the effect of fluorocarbon radicals. The ionic species in a CF$_4$ plasma are mainly CF$_3^+$, in addition to less fluorinated ions. Due to difficulties in making a clean, high-flux beam of CF$_3^+$, a beam of Ar$^+$ ions was used in the UHV apparatus as the source of energetic ions. This substitution has been made in past studies of ion-enhanced etching of SiO$_2$ with XeF$_2$ to decouple the effects of ion inertia and ion chemistry.[15,19,23,24] Tu et al.[15] studied SiO$_2$ sputtering with CF$_3^+$ ions and Ar$^+$ ions in the presence of XeF$_2$ and found that the CF$_3^+$ ions were twice as effective as Ar$^+$ in etching SiO$_2$, but that the effectiveness of both ions showed the same dependence on the flux of XeF$_2$. Winters[23] found that the products from the sputtering of SiO$_2$ in the presence of XeF$_2$ were relatively independent of the type of ion (Ar$^+$ or CF$_3^+$) used to bombard the surface.

This paper describes an investigation of the individual and combined effects of CF$_2$ and F on the Ar$^+$ ion sputtering yield of SiO$_2$. The flux levels in these experiments are representative of the flux levels in the plasma environment. Simple models involving the ion-enhanced adsorption of CF$_2$ and F were derived from a much larger set of possible surface reactions and ion enhancement mechanisms. These simple, two-parameter models capture the major features of the ion-enhanced etching of SiO$_2$.

II. EXPERIMENTAL

The experimental apparatus used for these studies has been described in detail elsewhere.[25] A schematic of the system is provided in Fig. 1. The SiO$_2$ sample can be simultaneously exposed to three separately controlled beams. The beams used in this work include an Ar$^+$ ion beam generated in a Kaufman ion source, a difluorocarbene (CF$_2$) radical beam generated by pyrolysis of hexafluoropropylene oxide (HFPO), and an atomic fluorine (F) beam generated by a microwave discharge of F$_2$ and Xe. The sample temperature is measured and controlled with a thermocouple and stainless-steel heating filament. The etching rate of SiO$_2$ films is measured by laser interferometry at a 45° angle with the surface [Fig. 1(a)]. The sample is mounted to a transfer assembly, which insures alignment of the sample to the beams and
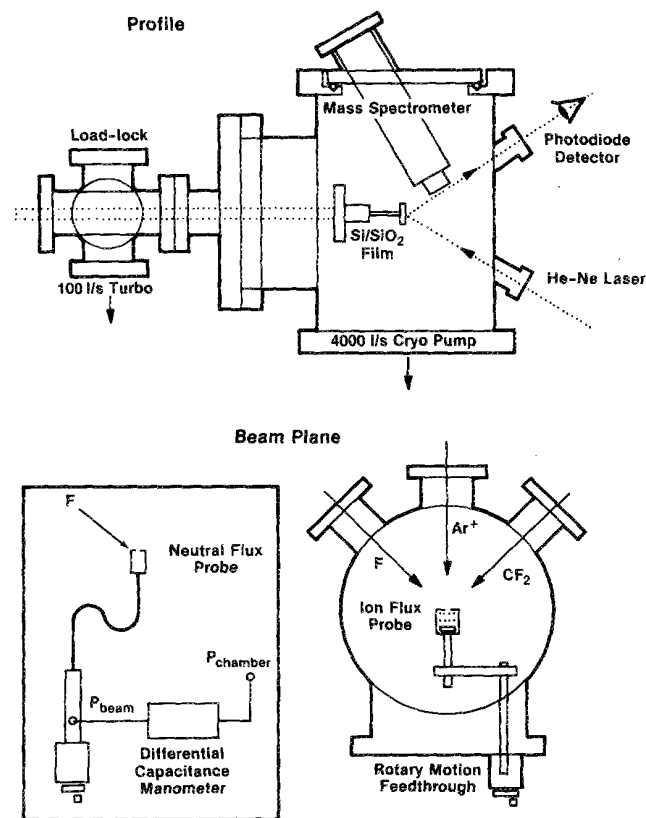

FIG. 1. The experimental apparatus. The profile view shows the laser interferometry and line-of-sight mass spectrometer. The beam plane view shows the beams and the two flux probes (retarding grid analyzer and pitot tube) which can be rotated into the sample position.

provides electrical connection to the thermocouple and stainless-steel heating filament.

A Faraday cup with retarding grids measures the ion flux and energy distribution at the sample position. With the sample removed, the cup is rotated into place on a rotary feedthrough, as shown in Fig. 1(b). The flux of neutral species is measured with a pitot tube that is also moved into the sample position on a rotary feedthrough. The pressure differential in the pitot tube is measured with a differential baratron.

A quadrupole mass spectrometer is mounted on the upper flange and can be used for analysis of the beams or for analysis of etching products from the surface of the sample. The ionizer is equipped with a line-of-sight shield such that the signal from background gas is minimized.

The chamber is pumped with an 8 in. cryogenic pump and the load lock is pumped with a turbomolecular pump. The base pressure in the chamber is typically around 5×10^{-8} Torr after 5–10 h of pumping; the chamber is frequently brought up to atmospheric pressure to replace the filaments in the ion source. The gases used are research purity ($> 99.9995\%$) Ar, research purity ($> 99.99\%$) Xe, technical grade ($> 97.0\%$) F$_2$, and HFPO (98.83%). Gas flow rates are set with needle valves, based on pitot tube measurements. The SiO$_2$ samples are 2-μ-thick sputtered quartz films on Si substrates.

The Ar$^+$ and F sources were previously described in detail.[25] A monoenergetic beam of Ar$^+$ ions is created with a Kaufman ion source with a 1 cm^2 nominal beam cross section. The F beam is created by the microwave discharge dissociation of F$_2$ in an alumina tube. The F$_2$ is mixed with about 2 sccm of Xe to maintain stability of the discharge. Mass spectrometric analysis indicates that dissociation of F$_2$ in this source is close to 100%.

The CF$_2$ beam was created from the pyrolysis of hexafluoropropylene oxide (HFPO)[26] in a resistively heated Pyrex tube. Knickelbein et al.[26] provided evidence that HFPO is completely dissociated at temperatures above 590 K in a pyrolysis tube with a residence time of 10 ms according to the reaction:

$$CF_3\text{–}CF\text{–}CF_2 \rightarrow CF_3\text{–}CF = O + CF_2. \qquad (1)$$
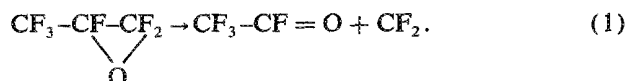
Knickelbein et al. monitored the extent of this reaction via laser-induced fluorescence (LIF) detection of CF$_2$. Since the pyrolysis tube used in this work is of different dimensions (straight, 3 mm inner diameter) than that used by Knickelbein et al. (nozzle geometry), it was important to characterize the cracking of HFPO as a function of tube temperature. The pyrolysis of HFPO was characterized by monitoring the mass spectrum of the products flowing out of the tube. The chamber pressure, due to HFPO flow, was 3×10^{-6} Torr (chamber base pressure was less than 8×10^{-8} Torr), which corresponded to an HFPO flow rate of about 0.2 sccm and a 10 ms residence time in the hot zone of the pyrolysis tube.

Quantitative mass spectrometric characterization of HFPO pyrolysis would require much effort due to its complicated cracking pattern, which includes CF$^+$, CF$_2^+$, and

CF$_3^+$, with the commonly used ionizer electron energy of 70 eV. Since CF$_2^+$ is a product of the electron impact of HFPO and CF$_3$CFO, as well as CF$_2$, at high ionizer energies, it is advantageous to choose an electron energy which ionizes the CF$_2$ radical, but which produces as little dissociation as possible of higher molecular weight species. Therefore, the ionizer electron energy was held at 20 eV (the minimum for the mass spectrometer) for the HFPO pyrolysis characterization. The appearance potential for the process

$$CF_2 + e^- \rightarrow CF_2^+ + 2e^- \qquad (2)$$

has been estimated at 13.3 eV.[27] Appearance potentials for the dissociative processes are unknown, but are expected to be several eV larger.

Figure 2 is a plot of the ratio of the CF$_2$ peak to the CF$_3$ peak versus temperature. The ratio was plotted to eliminate noise due to variations in the flow rate and base pressure during the series of readings. The ratio starts increasing at about 500 K, which corresponds to the minimum temperature at which Knickelbein et al.[26] could detect CF$_2$ radicals by LIF. The ratio of CF$_2$ to CF$_3$ has a sigmoidal shape with a knee at about 750 K. This saturation is at a significantly higher temperature than that detected by Knickelbein et al. (600 K),[26] attributable to a different hot-zone residence time and to the qualitative nature of the mass spectrometric analysis. The pyrolysis dependence on the HFPO flow rate was also investigated at 730 K with no significant change in the CF$_2$ to CF$_3$ signal ratio over a range of 0.2–0.6 sccm.

The qualitative results of the mass spectrometric characterization of the pyrolysis of HFPO in this apparatus indicated that pyrolysis was occurring with an efficiency close to 100%, based on the work of Knickelbein et al.[26] The temperature of the HFPO pyrolysis tube was held at 740–760 K
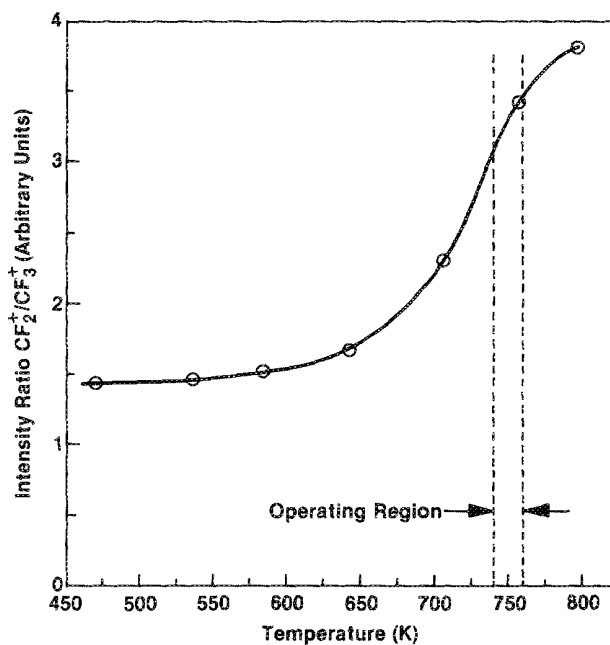

FIG. 2. Mass spectrometric intensity ratio of CF$_2^+$ to CF$_3^+$ during the pyrolysis of HFPO. The mass spectrometer ionizer energy was 20 eV.

for all studies in which a CF$_2$ flux was used.

One must also be concerned with the effect of the CF$_3$CFO and any unreacted HFPO on the etching reaction. In the case of HFPO, the etching of SiO$_2$ by Ar$^+$ ions was monitored in the presence of various flux levels of room-temperature HFPO (Fig. 3). The physical sputtering rate was unaffected by the impingement of HFPO, so it was reasonable to assume that the HFPO had a negligible sticking probability on SiO$_2$. This was not surprising as Winters[28] determined that the sticking probability of molecular species like CF$_4$, CF$_3$H, and CF$_3$Cl is less than 10^{-7}. It was expected that the sticking probability of CF$_3$CFO was also negligible since it is a stable molecular species. Thus, it was assumed that the only species in the pyrolyzed HFPO beam that can affect the etching of the SiO$_2$ was the CF$_2$ radical.

CF$_2$ fluxes of up to 5×10^{16}/cm^2 s were obtainable; at higher fluxes back-mixing of fluorocarbon species into the Kaufman ion source affected the quality of the data. This flux level compares very well with the typical CF$_2$ flux striking the surface in a CF$_4$ plasma. LIF measurements[29] indicate that the CF$_2$ concentration in a CF$_4$ plasma is on the order of 10^{12}/cm^3, which corresponds to a surface flux of about 10^{16}/cm^2 s at 300 K. F fluxes of up to 2×10^{17}/cm^2 s (corresponding to 1.4×10^{13}/cm^3 in the plasma environment) and Ar$^+$ fluxes of up to 3×10^{15}/cm^2 s at 250 eV (corresponding to 0.5 mA/cm^2 in the plasma environment) were obtainable.

III. RESULTS AND DISCUSSION

In the first series of experiments, the ion-enhanced etching of SiO$_2$ in the presence of CF$_2$ was examined. The results are shown in Fig. 4, where the etching yield (the number of SiO$_2$
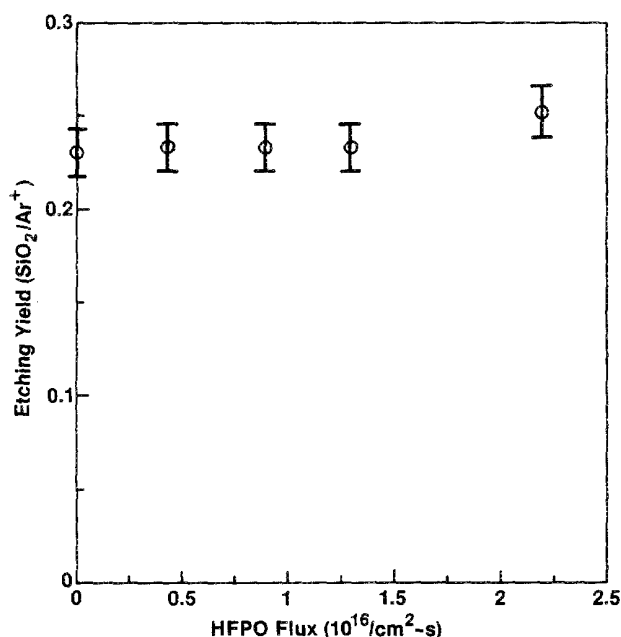

FIG. 3. Dependence of the etching yield on the flux of room-temperature HFPO showing that HFPO has negligible interaction with the ion-bombarded surface.
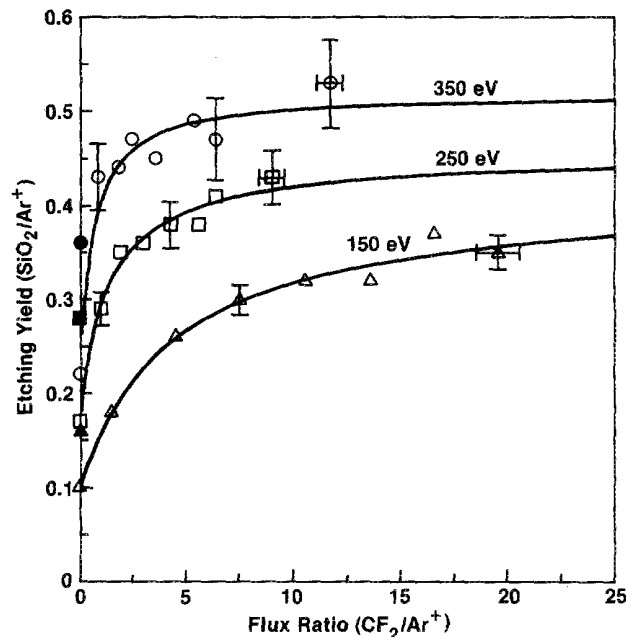

FIG. 4. The etching of SiO$_2$ with Ar$^+$ ions in the presence of CF$_2$ at ion energies of 150, 250, and 350 eV. The error bars indicate estimated uncertainty in instrument readings. Filled symbols indicate baseline sputtering in a "dirty" system. The solid lines are derived from the two-parameter model of Eq. (9).

molecules leaving the surface per incident Ar$^+$ ion) is plotted against the CF$_2$-to-Ar$^+$ flux ratio for ion energies of 150, 250, and 350 eV. The yields with a clean system and no CF$_2$ flux are in reasonable agreement with previously published values.[17,18] After the system was exposed to HFPO, the apparent baseline physical sputtering rates were higher than in a well-cleaned system due to residual fluorocarbon contamination in the ion gun (filled symbols in Fig. 4). Etching of the SiO$_2$ was not observed with a CF$_2$ flux in the absence of ion bombardment. Previous studies have shown that CF$_2$ adsorbs to some extent on the surface of both virgin and sputtered SiO$_2$, but does not etch the SiO$_2$ surface[10] (see discussion above). We saw no indications of polymer film deposition on the surface by the CF$_2$. Evidence for the lack of a polymer film was that the SiO$_2$ etching rate immediately returned to its baseline level after the CF$_2$ flux was terminated.

It is evident in Fig. 4 that the Ar$^+$ etching yield is enhanced by the flux of CF$_2$ on the surface; at an ion energy of 150 eV, the saturated yield with CF$_2$ is over three times the physical sputtering yield. The yields tend toward an asymptotic value as the ratio of CF$_2$ to Ar$^+$ increases; i.e., increasing amounts of CF$_2$ have less effect on the yield. It appears that saturation of the yield occurs at lower flux ratios for higher energy ions. This last feature is counter-intuitive in that one would expect higher energy ions to be more efficient at removing products from the surface, causing saturation to occur at higher flux ratios. An explanation of this behavior is that the CF$_2$ sticking probability increases with ion energy. The more damaged surface, expected with higher energy ion bombardment, may offer more adsorption sites and increase

DOCKET ALARM

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.