Effects of Ar and O$_2$ additives on SiO$_2$ etching in C$_4$F$_8$-based plasmas

Xi Li, a) Li Ling, Xuefeng Hua, Masanaga Fukasawa, b) and Gottlieb S. Oehrlein c)

Department of Materials Science and Engineering and Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland 20742-2115

Marcos Barela and Harold M. Anderson
Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico 87131

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Gas mixtures based on C$_4$F$_8$ are promising for the development of high-performance SiO$_2$ plasma etching processes. Measurements of important gas phase species, thin film etching rates and surface chemistry changes were performed for inductively coupled plasmas fed with C$_4$F$_8$/Ar and C$_4$F$_8$/O$_2$ gas mixtures. The addition of Ar to C$_4$F$_8$ causes a strong increase of the plasma density relative to that of pure C$_4$F$_8$ (by up to a factor of 4× at 90% Ar). For O$_2$ addition the changes in plasma density are small up to 90% O$_2$ relative to pure C$_4$F$_8$. Infrared laser absorption spectroscopy was used to determine the absolute densities of neutral CF, CF$_2$ and COF$_2$ radical species as a function of the gas composition. The densities of CF and CF$_2$ were enhanced for certain operating conditions when Ar was added to C$_4$F$_8$ as long as the amount of Ar remained below 20%. For instance, the partial pressure of CF was 0.1 mTorr for a 20 mTorr 1400 W source power discharge for pure C$_4$F$_8$, and increased to 0.13 mTorr at 20% Ar. Above 20% Ar it decreased, roughly following the gas dilution. The CF$_2$ partial pressure was about 5 mTorr for the same conditions, and increased by about 10% at 20% Ar. Above 20% Ar the CF$_2$ partial pressure decreased roughly linearly with the amount of Ar added, to about 2 mTorr at 50% Ar. Of particular interest was the analysis of the difference in behavior of CF, CF$_2$ and COF$_2$ partial pressures over SiO$_2$ and Si surfaces, with and without rf bias power (in the latter case a self-bias voltage of ~100 V was used). For pure C$_4$F$_8$ discharges at 20 mTorr and 1400 W inductive power without rf bias the partial pressures of CF, CF$_2$ and COF$_2$ radicals are comparable over SiO$_2$ and Si surfaces. Upon applying a rf bias, the CF$_2$ partial pressure over a SiO$_2$ surface is reduced much more strongly than for a Si surface. The overall reduction appears to be consistent with the relative SiO$_2$/Si etch rate ratios observed for these conditions. These results indicate that CF$_2$ is consumed during the etching of SiO$_2$ and Si. We also measured fluorocarbon deposition rates without rf bias and etching rates of blanket SiO$_2$, silicon, resist and deposited fluorocarbon films as a function of the rf bias and feed gas composition. Important differences in the response of the etching rates of those materials upon the addition of O$_2$ and Ar to C$_4$F$_8$ were observed. In particular, we show that the SiO$_2$/Si and SiO$_2$/resist etching selectivities can be doubled by adding up to 90% Ar to C$_4$F$_8$, without inducing an unacceptably large reduction of the SiO$_2$ etching rate. The change in etch rate ratios is at least in part due to strong surface chemical changes seen for Ar-rich fluorocarbon gas mixtures. The surface chemical changes of Si and SiO$_2$ surfaces were investigated by real-time ellipsometry and x-ray photoelectron spectroscopy.

A strong reduction of the fluorine content of the fluorocarbon steady-state layer and an increase in thickness is seen when up to 90% Ar was added to C$_4$F$_8$, and this coincides with an increase of the SiO$_2$/Si etching selectivity. The change in fluorocarbon surface chemistry can be explained by the strongly increased ion/neutral flux ratio that is characteristic of Ar-rich C$_4$F$_8$/Ar gas mixtures.

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I. INTRODUCTION

Fluorocarbon-based plasma etching of SiO$_2$ and low dielectric constant films is an important processing step in integrated circuit manufacturing. One of the most widely employed plasma sources for this is the inductively coupled plasma source. Process optimization in inductively coupled fluorocarbon plasmas has been found to be challenging due to the complexity of the fluorocarbon plasma etch mechanism. Gas mixtures based on C$_4$F$_8$ are a promising etching chemistry for high-performance SiO$_2$ etching. Because of the usefulness of C$_4$F$_8$ gas, ion fluxes and energies, 1 mechanisms of C$_4$F$_8$ dissociation, 2 the molecular composition of deposited films, 3 and radical kinetics of polymer film deposition 4 in pure C$_4$F$_8$ plasma have been investigated. Spatial distributions of absolute CF and CF$_2$ radical densities in electron cyclotron resonance (ECR) plasmas of C$_4$F$_8$ were also studied. 5,6 SiO$_2$ etching and SiO$_2$ etching selectivities to silicon and Si$_3$N$_4$ in pure C$_4$F$_8$ plasma have been reported. 7

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a)Electronic mail: lixi@glue.umd.edu
b)Electronic mail: masanaga.Fukasawa@jp.sony.com
c)Electronic mail: oehrlein@glue.umd.edu
a UHV-compatible processing chamber with a base pressure of \(5 \times 10^{-6}\) mTorr. The roof of the reactor is a 19.6 mm thick, 230 mm diam quartz window on which a 160 mm diam planar coil is located. The coil is powered by a 0–2000 W power supply at 13.56 MHz. Matching of the plasma source is achieved through a modified L-matching network configuration. This setup allows inductive plasma generation below the quartz window. All data were taken at matching network settings that allow the most inductive coupling to the system, resulting in minimal window erosion. The total gas flow into the reactor was set at 40 sccm at operating pressures of 6 and 20 mTorr. These pressures were obtained using an automatic throttle valve located at the exit of the pumping line of the reactor.

The experimental data were obtained in a reactor that was preconditioned in the following fashion. First, a 40 sccm \(O_2\) plasma was run at 1000 W inductive power and 10 mTorr operating pressure. This \(O_2\) treatment served a dual purpose; (1) removal of fluorocarbon material deposited during prior experiments on the reactor wall and/or quartz window and (2) heating of the reactor walls to a stable temperature.\(^{12}\) The reactor cleanliness during the \(O_2\) preconditioning step was monitored using optical emission spectroscopy and quadrupole mass spectrometry.

After \(O_2\) pretreatment had been completed, a set of measurements was performed in such a fashion that experiments at conditions without deposition on the quartz coupling window preceded experiments with deposition on the window. It is of importance to perform experiments consistently in this fashion, because of hysteresis effects that may otherwise occur.

The wafers that were processed are located on a wafer holder that was cooled to 10°C. The distance between the wafer and the induction coil is 8.5 cm. The chuck is powered through a II-matching network from a variable frequency (0.4–40 MHz) rf power supply (0–300 W). This setup allows biasing of the wafer to be independent of the plasma generated, thus enabling control of the ion energy that is separate from plasma generation. For experiments in this project the sample bias power was varied up to a maximum of 250 W at a fixed frequency of 3.7 MHz. The self-bias voltage was measured using a high-voltage wafer probe connected to an oscilloscope and for all gas mixing experiments it was controlled to \(-100\) V.

**B. Diagnostics**

The experimental results given in this article are based on Langmuir probe measurements, real-time, \textit{in situ} ellipsometry (fluorocarbon deposition rates, thin film etching rates, and characterization of modified surface layers), infrared absorption measurements of CF, CF\(_2\), and COF\(_2\) radicals, and x-ray photoelectron spectroscopy analysis of plasma-etched surfaces.

1. Ellipsometry

Samples placed at the center of the wafer can be monitored by an \textit{in situ} He–Ne (632.8 nm) rotating compensator ellipsometer (RCE) in a polarizer-compensator-sample-analyzer (PCSA) configuration.\(^{13}\) He–Ne ellipsometry is used for real-time etch and deposition rate measurements and monitoring of surface modifications on semi-infinitely thick Si substrates.

2. Infrared laser absorption spectroscopy

The infrared laser absorption spectroscopy (IRLAS) setup used in this work is a homemade setup that was established at the University of New Mexico. The infrared laser in this setup is a liquid nitrogen cooled lead-salt diode laser (Laser Photonics). Using a setup of various planar and elliptical mirrors that were positioned on an optical table and on the reactor, an infrared laser beam is double passed through the reactor and focused onto a fast photovoltaic HgCdTe liquid nitrogen cooled detector. The windows on the reactor through which the infrared laser beam is transmitted are made of barium fluoride (BaF\(_2\)), which is transparent in the wavelength/wave number range of interest. The windows are
mounted 5° off axis to prevent multiple reflection effects. In order to align the optical setup, a He–Ne laser, that was co aligned with the diode laser, is used.

The wavelength/wave number at which the laser emits light is dependent on the temperature of and the current through the diode. The laser temperature is adjusted using a temperature controller (DRC-91CA, LakeShore). The laser current is regulated using a current controller (LDX-3525, ILX Lightwave), and is ramped at 50 Hz to sweep the laser emission over an approximately 0.2 cm⁻¹ frequency/wave number range. Wavelength/wave number calibration is performed by inserting a reference gas into the reactor. In this work, ammonia (NH₃) was used as the reference gas since it has absorption lines of known line strength at known wave numbers in the range of interest.

In order to increase the sensitivity of the IRLAS method, a wavelength modulation approach is employed. The 50 Hz sweep signal which selects the wavelength/wave number emitted is modulated with a small 50 kHz sinusoidal wave. The signal detected, which will be modulated with the same 50 kHz frequency, is fed into a lock-in amplifier (SR 830 DSP, Stanford Research Systems). The lock-in amplifier was set to trigger the second harmonic of the modulation frequency, i.e., 100 kHz. The signal demodulated by the lock-in amplifier is displayed on a storage oscilloscope that is interfaced to a computer that is used for data collection. The data collected in the above fashion essentially represent the second derivative of the absorption spectrum. This approach and the methodology of analysis have been described by Schaepkens et al.¹⁴

### 3. X-ray photoelectron spectroscopy

Detailed surface chemical information for etched crystalline silicon and SiO₂ samples was obtained using x-ray photoelectron spectroscopy (XPS). After real-time ellipsometry surface analysis, the inductive power and, within 1 s, the rf bias power, were turned off. This procedure minimizes changes in surface modification that are present during the etching process. The samples were transferred to a Vacuum Generators ESCA Mk II analysis chamber. Photoelectrons were emitted using a nonmonochromatized Mg Kα x-ray source (1253.6 eV). Survey spectra and high resolution spectra of C(1s), Si(2p), F(1s) and O(1s) electron emission were obtained under two emission angles, 70° and 0° with respect to the sample normal. The spectra presented in this article were obtained at 20 eV pass energy.

### III. RESULTS AND DISCUSSION

#### A. Ion currents

Figure 2 shows the dependence of the ion current density on the amount of Ar and O₂ added to C₄F₈. The plasma was operated at 1400 and 600 W inductive power, pressures of 6 and 20 mTorr and total gas flow of 40 sccm. The ion current was measured using a Langmuir probe. A significant increase in the ion current is observed when Ar is added (atomic and electropositive gas). On the other hand, the ion current remains almost unchanged when O₂ is added.

#### B. Infrared laser absorption measurements

Figure 3 shows second derivative IRLAS spectra obtained with inductively coupled plasmas at 1400 W inductive power and 6 and 20 mTorr operating pressure fed with 40 sccm of C₄F₈. For comparison the spectrum obtained with NH₃ gas at 30 mTorr (no plasma) is also shown. The peak position of the different species is indicated. It can be observed that at this condition there is a large variation in CF and CF₂ absorption for different pressures.

Figure 4 shows second derivative IRLAS spectra obtained with inductively coupled plasmas at 1400 W inductive power and 20 mTorr operating pressure fed with 40 sccm of 20% C₄F₈/O₂ and C₄F₈/Ar plasmas and NH₃ gas at 30 mTorr. Figure 4 demonstrates the relative magnitude of the changes in CF, CF₂ and COF₂ intensity as we switch from an Ar additive to an O₂ additive.

Figures 5–7 show the densities of CF, CF₂ and COF₂ calculated from absorption spectra obtained with C₄F₈,
C₄F₈/O₂ and C₄F₈/Ar plasmas operated at a total gas flow of 40 sccm, 20 mTorr pressure, and 600 and 1400 W inductive power as a function of the amount of O₂ or Ar added, respectively. The labels “fluorocarbon deposition,” “fluorocarbon etch” and “Si etch” shown in Figs. 5–7, respectively, refer to the following operating conditions: For “fluorocarbon deposition” (Fig. 5) no sample bias was applied and fluorocarbon film deposition took place on the sample. For “fluorocarbon etch” (Fig. 6) a sample bias of −100 V was applied and the passively deposited fluorocarbon film was removed. For “Si etch” (Fig. 7) a sample bias of −100 V was applied and steady-state Si etching took place. We note from Figs. 5–7 that the densities of CF and CF₂ are higher with the Ar additive than with the O₂ additive. Small amounts of Ar added to a C₄F₈ plasma can enhance the CF and CF₂ radical densities relative to those of pure C₄F₈ for 1400 W source power. The CF₂ partial pressure is about an order of magnitude greater than that of CF. A comparison of Figs. 5(b) and 6(b) shows that adding rf bias causes a reduction in CF₂ for C₄F₈/Ar discharges. We will show below that Ar addition to C₄F₈ is useful for highly selective SiO₂ etching processes since it enhances the selectivity of SiO₂ etching relative to silicon and resist etching.

**Fig. 3.** Second derivative absorption spectra in C₄F₈ plasmas at 40 sccm gas flow, 1400 W inductive power and 6 and 20 mTorr operating pressures. For comparison, the spectrum obtained with 30 mTorr NH₃ gas (no plasma) is shown.

**Fig. 4.** Second derivative absorption spectra of C₄F₈/20% O₂ and C₄F₈/20% Ar plasmas at 40 sccm gas flow, 1400 W inductive power and 20 mTorr operating pressure, and 30 mTorr NH₃ reference gas (no plasma).

**Fig. 5.** Densities of CF, CF₂ and COF₂ calculated from absorption spectra obtained at 40 sccm gas flow for 20 mTorr pressure and 600 and 1400 W inductive power for the C₄F₈/O₂ and C₄F₈/Ar fluorocarbon deposition process as a function of the percentage of O₂ and Ar added.

**Fig. 6.** Densities of CF, CF₂ and COF₂ calculated from absorption spectra obtained at 40 sccm gas flow for 20 mTorr pressure and 600 and 1400 W inductive power for the C₄F₈/O₂ and C₄F₈/Ar fluorocarbon etching process as a function of the percentage of O₂ and Ar added.
The COF$_2$ results show very different trends for O$_2$ and Ar additives. The COF$_2$ density initially decreases when small amounts of O$_2$ are added to C$_4$F$_8$, and then clearly increases as the amount of O$_2$ is raised above 20%. On the other hand, the COF$_2$ density increases slightly and then decreases slightly as the amount of Ar in C$_4$F$_8$/Ar is raised.

Figure 8 shows the influence of the thin film material in contact with the plasma on the densities of CF, CF$_2$ and COF$_2$ calculated from absorption spectra. The data were obtained with C$_4$F$_8$, C$_4$F$_8$/30% O$_2$, and C$_4$F$_8$/30% Ar plasmas operated at 40 sccm gas flow, 20 mTorr pressure, and 1400 W inductive power for Si and SiO$_2$ surfaces, respectively. An important result shown in Fig. 8 is a significant reduction of CF$_2$ for C$_4$F$_8$ and C$_4$F$_8$/30% Ar discharges over a SiO$_2$ surface when a rf bias is applied. The reduction of CF$_2$ is characteristic of the SiO$_2$ surface and not seen to this extent for the Si surface.

C. Fluorocarbon deposition and etching data

In fluorocarbon gas mixtures, fluorocarbon deposition on surfaces occurs along with fluorocarbon etching. To provide insight as to the relative changes of these processes with the gas composition, the fluorocarbon deposition and etching rates were determined as a function of the gas additive. Figures 9 and 10 display the fluorocarbon deposition and etching rates without rf bias and 200 V self-bias voltage, respectively.

Figure 9 shows the fluorocarbon deposition rate versus O$_2$ and Ar gases added for 40 sccm gas flow, 20 mTorr pressure, and 1400 W inductive power for Si and SiO$_2$ surfaces, respectively.
The fluorocarbon deposition rate is always higher with the Ar additive than with the O₂ additive. We observe an overall trend towards lower fluorocarbon deposition rates as Ar and O₂ are added to C₄F₈ at 600 W inductive power and 20 mTorr processing pressure. This is expected because of the reduced supply of C₄F₈ molecules to the reactor as increasing proportions of Ar and O₂ are added to C₄F₈. The deposition rate vanishes when more than 50% O₂ was added. The deposition rates are higher for 1400 W inductive power than for 600 W inductive power. In addition, at low proportions of Ar in C₄F₈/Ar, an increase in the fluorocarbon deposition rate is observed relative to in pure C₄F₈ for 1400 W inductive power. This effect is also seen for O₂ addition, although it is weaker. At 600 W inductive power this increase is not observed.

The comparison of the Ar and O₂ gas addition experiments indicates that both ion bombardment enhanced fluorocarbon deposition and oxidation of fluorocarbon at the substrate surface appear to be important in explaining these data. The fluorocarbon deposition rates as a function of the amount of additive show similar trends as the densities of the CF and, to a lesser extent, CF₂ radicals with O₂ and Ar gas additives. This supports the notion that CF and CF₂ radicals play an important role in the fluorocarbon deposition process. Because of the different capabilities of etching SiO₂, Si and resist surfaces in gasifying deposited fluorocarbon films, the above processes will influence the SiO₂/Si and SiO₂/resist etch selectivity that can be achieved.

Figure 10 shows the corresponding fluorocarbon etching rates at –100 V self-bias voltage. At low inductive power (600 W), the etching rates increase gradually for both O₂ and Ar. Above 70% O₂, the etch rate increases more rapidly in the case of O₂. For Ar a monotonic decrease of the etch rate is measured with an increase in Ar content above 70%. At high inductive power (1400 W), the behavior is quite different: When Ar is added, a monotonic decrease of the etch rate is measured for all Ar levels. For O₂ addition a small decrease of the etching rate is observed when up to 40% O₂ is added. When more than 60% O₂ is added, the fluorocarbon etching rate more than doubles relative to that of pure C₄F₈.

**D. Effects of adding Ar and O₂ to C₄F₈ on SiO₂ and Si etching**

1. **SiO₂ etching behavior**

Figure 11 shows the SiO₂ etching rate measured as a function of rf bias power and self-bias voltage for pure C₄F₈ at 600 and 1400 W inductive power, 20 mTorr pressure and total gas flow of 40 sccm. It is well known that when plotting the etching rate of SiO₂ as a function of rf bias power in high-density fluorocarbon plasmas, three different etching regimes can be distinguished. At low rf powers, net fluorocarbon deposition takes place. As the rf bias power is increased, the deposition rate decreases rapidly due to etching fluxes coming off the surface until the threshold of net substrate etching is reached. At this point the deposition flux at the surface is equal to the etching flux. Once the bias voltage is...
increased beyond this value, etching becomes greater than deposition, and net substrate etching takes place. The etch rate increases rapidly with an increase of rf bias power. In this fluorocarbon suppression regime, steady-state etching of the oxide occurs through a fluorocarbon layer which is present on the SiO2 surface.15 Since the steady-state fluorocarbon film is comparable to the typical ion penetration depth at these ion energies (~1–2 nm), the SiO2 chemical sputtering rate is suppressed, and the etch rate of SiO2 is strongly dependent on the thickness of the fluorocarbon film. At high enough self-bias voltages the fluorocarbon film is so thin that direct ion induced chemical etching dominates the etching of SiO2.

The behavior data of the etch rate in Fig. 11 are representative of the qualitative behavior of the etching rates of other materials as a function of the rf bias as well. The absolute magnitude of the etching rate in the high-voltage regime varies strongly according to the material, and reflect differences in thickness of the steady-state fluorocarbon films present during etching on the surfaces of these materials. In the following we report the etching rates of different materials as a function of the gas composition. For the comparison of the etching rates using different gas mixtures, we employed a fixed self-bias voltage of ~100 V. Subsequently, Si and SiO2 surface analysis data obtained for the same conditions will be reported.

2. Variation of the SiO2 etching rate with Ar and O2 addition

The dependence of the SiO2 etching rates at a fixed self-bias voltage of ~100 V on the gas composition in C4F8/Ar and C4F8/O2 gas mixtures at 20 mTorr pressure and inductive powers of 600 and 1400 W is shown in Fig. 12. This etching condition is above the fluorocarbon suppression regime. We see that the etching rate (ER) is greater with the Ar gas additive than with the O2 gas additive for both 600 and 1400 W inductive power. Whereas at 1400 W power a monotonic decrease of the SiO2 ER is seen for both Ar and O2 additives, at 600 W inductive power, for both the O2 and Ar additives, the etching rate increases for low additive percentages. In the case of the O2 gas additive the etch rate drops off monotonically with an increase of O2 above 40%. For Ar the SiO2 etch rate continues to increase above 40% gas addition and only starts to decrease when the Ar content is 70% and greater. Overall, we conclude that for C4F8/Ar the SiO2 etching rate remains high up to rather high Ar concentrations, whereas for C4F8/O2 gas mixtures a decrease of the SiO2 etching rates occurs for smaller amounts of O2 added.

3. Variation in polycrystalline Si etching rate with Ar and O2 additions

Figure 13 shows polysilicon etching rates as a function of the gas composition. For both C4F8/Ar and C4F8/O2 a monotonic increase of the Si etching rates with an increase in the proportion of Ar or O2 is seen up to 50% for either gas additive at 600 W inductive power. Above 50%–60% gas addition, the Si etching rates decrease. For C4F8/O2 a stronger increase of the Si etching rate is observed as a function of gas addition than for C4F8/Ar. The etch rate at 50% O2 is 3× that measured for pure C4F8. At 1400 W inductive power, the Si etch rate shows a similar trend as a function of the amount of O2 added to that observed for C4F8/O2 at 600 W inductive power. For C4F8/Ar gas mixtures and 1400 W source power the Si etch rate decreases monotonically with the Ar content.

E. Effect of gas additives on resist etching

Figure 14 shows the resist etching rate as a function of the gas composition. The etch rate trends are similar to those obtained with the fluorocarbon material. At a source power feed of 600 W, for both Ar and O2 additives a slight increase of the resist etching rates is seen up to 40% gas addition. The etching rate increases sharply when the amount of O2 is increased to above 40%. For Ar addition, the etching rate de-
creases when more than 70\% Ar was added at 600 W source power. At 1400 W the resist etch rate decreases monotonically as the amount of Ar is increased. At all gas compositions, the resist etching rate in \( \text{C}_4\text{F}_8 /\text{Ar} \) gas mixtures is lower than that for \( \text{C}_4\text{F}_8 /\text{O}_2 \) gas mixtures.

**F. Etching selectivity**

In Fig. 15 the etching selectivities of \( \text{SiO}_2 /\text{Si} \) and \( \text{SiO}_2 /\text{resist} \) are shown as a function of the percentage of \( \text{O}_2 \) or Ar added to \( \text{C}_4\text{F}_8 \). The addition of Ar leads to an increase of the \( \text{SiO}_2 /\text{Si} \) and \( \text{SiO}_2 /\text{resist} \) etching selectivities. The strong increase of the \( \text{SiO}_2 /\text{resist} \) etch rate ratio observed at 90\% Ar in \( \text{C}_4\text{F}_8 \) appears useful since the \( \text{SiO}_2 \) etch rate at this condition is comparable to that measured for pure \( \text{C}_4\text{F}_8 \) at 600 W source power.

For \( \text{O}_2 \) addition, the \( \text{SiO}_2 /\text{Si} \) and \( \text{SiO}_2 /\text{resist} \) etching selectivities first decrease nearly universally as the amount of \( \text{O}_2 \) is increased. Only at a very high percentage of \( \text{O}_2 \) addition does the \( \text{SiO}_2 /\text{Si} \) etch rate ratio increase. This coincides with very low \( \text{SiO}_2 \) etching rates, and the \( \text{SiO}_2 /\text{resist} \) selectivity is dramatically lowered at high percentages of \( \text{O}_2 \) addition, thereby reducing the technological usefulness of this observation.

**G. Surface analysis data**

Section III F showed that the addition of Ar to \( \text{C}_4\text{F}_8 \) enables increased \( \text{SiO}_2 /\text{Si} \) and \( \text{SiO}_2 /\text{resist} \) etching selectivity. To obtain information on changes in the surface condition and chemistry as a result of adding Ar, both real-time ellipsometry and subsequent XPS analysis were performed with plasma etched polycrystalline silicon and \( \text{SiO}_2 \) samples. The changes in silicon etching behavior reported above, in particular, are expected to be mirrored in the behavior of the steady-state fluorocarbon film thickness that exists during etching on the silicon surface.

In Figure 16 we display the ellipsometrically measured net thickness of the transparent surface layer formed on Si during plasma etching (shown by XPS to be a fluorocarbon layer except when a very high percentage of \( \text{O}_2 \) was added). The addition of Ar to \( \text{C}_4\text{F}_8 \) leads to thicker steady-state fluorocarbon layers on Si, especially at higher percentages of added Ar. When \( \text{O}_2 \) up to 60\% is added to \( \text{C}_4\text{F}_8 \), a reduction in the fluorocarbon film thickness is observed. (The increase in film thickness observed by ellipsometry at a higher percentage of \( \text{O}_2 \) added is attributed to the formation of \( \text{SiO}_2 \) on Si; the \( \text{CF}_x \) deposition rate is zero when more than 50\% \( \text{O}_2 \) is added; see Fig. 9.)

For XPS analysis, Si and \( \text{SiO}_2 \) samples were etched in pure \( \text{C}_4\text{F}_8 \), \( \text{C}_4\text{F}_8/20\% \text{Ar} \), \( \text{C}_4\text{F}_8/40\% \text{Ar} \), \( \text{C}_4\text{F}_8/60\% \text{Ar} \), and
C$_4$F$_8$/80% Ar plasmas using 600 W inductive power, 20 mTorr pressure, 40 sccm gas flow rate and 2100 V bias voltage for 1 min. XPS analysis performed with relatively thick ~200 nm passively deposited fluorocarbon films quantified the surface contamination as approximately 1% oxygen and 0.5% silicon. The effect of oxygen on the etching process for C$_4$F$_8$/Ar discharges was therefore neglected.

Figure 17 shows high resolution C(1s) electron emission spectra obtained with specimens prepared in the manner described above. The spectrum at the bottom of Fig. 17 was obtained with a 300-nm-thick fluorocarbon layer deposited on a Si sample using a 20 mTorr pure C$_4$F$_8$ plasma maintained at 600 W inductive power. The five C(1s) spectra above this trace were taken with crystalline silicon samples processed at a self-bias voltage of ~100 V, but different Ar concentrations. The effect of Ar addition is clearly visible as a significant reduction in the fluorine content of the fluorocarbon layer. The fluorocarbon film thickness increases at the same time. In the top part of Fig. 17, spectra obtained with SiO$_2$ samples etched at two different gas compositions are shown.

The comparison of the C(1s) data obtained with Si and SiO$_2$ surfaces after plasma etching in pure C$_4$F$_8$ shows that whereas for a Si surface CF$_2$ is the dominant group, for SiO$_2$ C–CF$_x$ is of highest intensity. This appears consistent with the strong difference in CF$_2$ gas phase concentration seen for these surfaces (see Fig. 8).

Figure 17 shows the highest C(1s) intensity at 80% Ar, suggesting a maximum of the CF$_x$ layer thickness on the Si surface and of the carbonaceous film thickness on the SiO$_2$ surface, respectively. This behavior is consistent with the ellipsometric analysis (seen in Fig. 18). Using the analysis method of Ref. 10, a careful evaluation of the XPS spectra and comparison with the ellipsometry data show that both ellipsometry and XPS lead to consistent steady-state fluorocarbon film thickness results (see Fig. 18).

The change in the fluorine content of the fluorocarbon films by adding Ar to C$_4$F$_8$ is presumably related to increased ion bombardment due to the higher plasma density of the C$_4$F$_8$/Ar discharge. Figure 19 shows the correlation between the F/C ratio decrease and the ion density increase.

The SiO$_2$/Si etching selectivity has been shown to be related to variation of the steady-state fluorocarbon film thickness on Si as process conditions are changed. This behavior is also seen here and is shown in Fig. 20. The selectivity increases with the fluorocarbon film thickness on the Si surface. For C$_4$F$_8$/Ar thicker fluorocarbon films are observed at high Ar percentages, and coincide with improved SiO$_2$/Si etching selectivity.
The study of CF, CF$_2$, and COF$_2$ concentrations as a function of the amount of O$_2$ and Ar added to C$_4$F$_8$. This increase appears to be related to the strong increase of the plasma density when Ar is added to C$_4$F$_8$. The study of CF, CF$_2$, and COF$_2$ concentrations as a function of the amount of O$_2$ added to C$_4$F$_8$ showed that the CF and CF$_2$ densities decreased, whereas that of COF$_2$ increased, except for the smallest amounts of O$_2$ added. In the latter case a slight increase of the CF and CF$_2$ densities was observed and this effect was also mirrored in the fluorocarbon deposition rate.

We also examined the dependence of the etching rates of SiO$_2$, poly-Si and resist on the amount of O$_2$ and Ar added to C$_4$F$_8$ during high-density plasma etching. For a higher percent of Ar addition and 600 W inductive power, the SiO$_2$ etching rate remains acceptably high and the SiO$_2$/Si and SiO$_2$/resist etching selectivities increase. The addition of O$_2$ to C$_4$F$_8$ reduces the SiO$_2$/Si and SiO$_2$/resist etching selectivity (except for the highest levels of O$_2$, where the SiO$_2$/Si selectivity increases).

Both ellipsometry and XPS showed that during steady-state etching the silicon surface is covered by a relatively thick fluorocarbon layer that varies from 2 to 4 nm. When the amount of Ar added to C$_4$F$_8$ was increased to 80%, a strong reduction of the fluorine content of this fluorocarbon layer and a concomitant increase of its thickness were observed. This increases the etching resistance of the steady-state fluorocarbon layer, and makes the increase in SiO$_2$/Si etching selectivity seen for Ar-rich C$_4$F$_8$/Ar gas mixtures understandable.

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