Fluorocarbon-based plasma etching of SiO$_2$: Comparison of C$_4$F$_6$/Ar and C$_4$F$_8$/Ar discharges

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A gas phase and surface chemistry study of inductively coupled plasmas fed with C$_4$F$_6$/Ar and C$_4$F$_8$/Ar intended for SiO$_2$ etching processes was performed. Adding Ar to those fluorocarbon gases results in a stronger increase of the ion current, by up to a factor of 5 at 90% Ar relative to the pure fluorocarbon gases. The fluorocarbon deposition rate is higher for C$_4$F$_6$/Ar than for C$_4$F$_8$/Ar, whereas the fluorocarbon etching rate is lower, and both quantities decrease as the amount of Ar is increased. For both C$_4$F$_6$/Ar and C$_4$F$_8$/Ar, the CF$_2$ density is more than an order of magnitude greater than the CF density. The CF$_2$ partial pressure decreases as more Ar is added to the C$_4$F$_6$/Ar plasmas. A comparison of these data with corresponding results obtained with C$_4$F$_8$/Ar shows that the CF$_2$ partial pressure in C$_4$F$_6$ is higher for Ar-lean gas mixture than for C$_4$F$_8$/Ar. This remains true up to 40% Ar. Above 40% Ar the CF$_2$ partial pressure in C$_4$F$_8$ is higher than for C$_4$F$_6$. The CF and COF$_2$ partial pressures in C$_4$F$_8$ are higher than for C$_4$F$_6$. The SiO$_2$ etch rate is higher for C$_4$F$_6$/Ar than for C$_4$F$_8$/Ar. This may be attributed in part to the higher F/C ratio of the steady-state fluorocarbon film formed on SiO$_2$ surfaces for C$_4$F$_6$/Ar which was determined by x-ray photoemission spectroscopy (XPS). The etching selectivity of SiO$_2$ over resist and silicon is increased by the addition of Ar to the fluorocarbon gases. Overall, the SiO$_2$/resist and SiO$_2$/Si etching selectivity are higher for C$_4$F$_6$/Ar (i.e., 4 and 9, respectively) at 90% Ar than for C$_4$F$_8$/Ar (i.e., 2 and 5, respectively) at 90% Ar and otherwise identical conditions. Both ellipsometry and XPS measurements show that the steady-state fluorocarbon layer thickness is greater for C$_4$F$_6$/Ar (~4 nm) than for C$_4$F$_8$/Ar (~2.8 nm). Argon addition leads to a strong decrease of the fluorine content of the steady-state fluorocarbon layers on both Si and SiO$_2$ surfaces relative to films produced in pure fluorocarbon discharges, and this effect is related to the increase of the SiO$_2$/Si and SiO$_2$/resist etching selectivity. © 2002 American Vacuum Society. [DOI: 10.1116/1.1517256]

I. INTRODUCTION

Perfluorocarbon gases like C$_2$F$_6$, CHF$_3$, and c-C$_4$F$_8$ contribute to the atmospheric greenhouse effect. These gases are important for plasma etching of SiO$_2$ in the semiconductor industry. The evaluation of candidate gases that can reduce the greenhouse effect and at the same time enable satisfactory SiO$_2$ etching is an important research topic. We have investigated C$_4$F$_6$ gas as a possible next generation etching gas and compared its process characteristics with those of C$_4$F$_8$ which has a high global warming potential (GWP). C$_4$F$_6$ has low GWP due to a much shorter lifetime of C$_4$F$_8$ in the atmosphere. The C$_4$F$_6$ molecule has two C=C bonds, see Fig. 1, which shows the hexafluoro-1,3-butadiene isomer. Since the dissociation of the C=C bond is five times easier than that of the C=C bond, the stability of the C$_4$F$_6$ molecule is less than that of cyclic C$_4$F$_8$. For the work reported in this article, we used hexafluoro-1,3-butadiene gas.

Frequently gas mixtures rather than pure fluorocarbon (FC) gases are being employed. The effect of adding Ar and O$_2$ to C$_4$F$_6$ and C$_4$F$_8$ was also studied in this work. The addition of Ar is thought to increase the importance of ion bombardment relative to neutral and direct reactive ion etching. The following measurements were performed in this work: Using a Langmuir probe we measured ion currents as a function of process parameters. Absolute densities of neutral CF, CF$_2$, and COF$_2$ radical species were determined using infrared laser absorption spectroscopy. In situ real-time ellipsometry was employed to determine fluorocarbon deposition and etching rates, SiO$_2$, resists, and silicon etching rates and steady-state fluorocarbon passivation layer thicknesses. The variation of the surface chemistry of the reaction layer formed on Si and SiO$_2$ with process parameters was investigated by X-ray photoelectron spectroscopy (XPS). For the etching and surface characterization work we describe primarily results obtained with C$_4$F$_6$/Ar discharges, since the addition of O$_2$ to fluorocarbon gases results in unacceptably high resist etching rates.

II. EXPERIMENTAL SETUP

A. Inductively coupled plasma source

The inductively coupled rf plasma (ICP) reactor of planar coil design used for these experiments is identical to that
employed previously. Briefly, the reactor consists of an ultrahigh vacuum (UHV) processing chamber with a base pressure of $5 \times 10^{-6}$ Torr. The roof of the reactor is a 19.6-mm-thick, 230 mm diameter quartz window on which a 160 mm 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 for inductive plasma generation below the quartz window. All data has been taken at the capacitor setting that allows for the most inductive coupling into the system, resulting in minimal window erosion.

The wafers that were processed were 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 the biasing of the wafer to be independent of plasma generation, enabling control of the ion energy separately from the plasma generation. For the experiments reported here, the conditions were 600 W inductive power, 6 or 20 mTorr operating pressure, 40 sccm total gas flow, and the sample bias was varied up to -100 V at a fixed frequency of 3.7 MHz. Pressure control was obtained using an automatic throttle valve located in the pumping line very close to the reactor’s outer wall.

For C$_4$F$_8$/Ar plasmas it is possible to maintain these discharges at arbitrary gas composition for inductive power from 400 to 1400 W. On the other hand, for pure C$_4$F$_8$ plasmas, or with C$_4$F$_8$/Ar discharges with a small amount of Ar, we were not able to maintain 20 mTorr operating pressure from 1000 to 1400 W inductive power at 40 sccm gas flow in our ICP reactor because of the rapid dissociation of C$_4$F$_8$. When a discharge was produced at 20 mTorr and high inductive power using C$_4$F$_8$-rich gas mixtures, the pressure would quickly drop to below 15 mTorr. For Ar-rich C$_4$F$_8$/Ar gas mixtures, this problem was not observed. The strong time dependence of Ar-lean C$_4$F$_8$/Ar discharges is the reason that we did not examine high inductive powers in that part of the work. Operation of fluorocarbon discharges at lower source power is also of great technological interest.

**B. Diagnostics**

Ion saturation current measurements were performed with a Langmuir probe. The conductive tip (area = 0.1 cm$^2$) of the Langmuir probe is located at the wafer center. Ellipsometry is used for measurements of fluorocarbon deposition rates, thin film etching rates, and characterization of modified surface layers. Silicon chips coated with thin films of SiO$_2$, polycrystalline silicon, and resist were placed at the center of a 125 mm diameter wafer and thermally bonded to the wafer. They were monitored using an in situ He–Ne (632.8 nm) rotating compensator ellipsometer (RCE) in a polarizer-compensator-sample-analyzer (PCS A) configuration.

Infrared laser absorption measurements of CF, CF$_2$, and COF$_2$ were performed up to an Ar content of 80% for both C$_4$F$_8$/Ar and C$_4$F$_6$/Ar discharges. The infrared laser absorption spectroscopy (IRLAS) setup used in this work is a homebuilt one 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, the infrared laser beam was double-passed through the reactor and focused on 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 are transparent in the wavelength/wave number range of interest. The windows were mounted at 5° off axis to prevent multiple reflection effects. In order to align the optical setup a He–Ne laser coaligned with the diode-laser was 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, Lake Shore). 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 approximately 0.2 cm$^{-1}$ frequency/wave number range. Wavelength/wave number calibration is performed by introducing a reference gas into the reactor. In this work, ammonia (NH$_3$) is used as a 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 emitted wavelength/wave number is modulated with a small 50 kHz sinusoidal wave. The detected signal, 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 is displayed onto a storage oscilloscope that is interfaced to a computer 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 previously been described.

Detailed surface chemistry information on etched crystalline silicon samples and similar samples overcoated with SiO$_2$ was obtained using x-ray photoelectron spectroscopy (XPS). After plasma processing, first the inductive power
and, within 1 s, the rf bias power, were turned off to maintain the surface modifications that are present during the etching process. This was verified using real-time ellipsometry. The samples were transferred in air to a Vacuum Generators ESCA Mk II surface 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 take-off 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. Effect of Ar addition to C₄F₆ and C₄F₈ on ion current density

Figure 2 shows the dependence of ion current density measured using a Langmuir probe on percentage Ar gas added to C₄F₆ and C₄F₈. A significant increase of the ion current is observed when a large amount of Ar is added (atomic and electropositive gas) for both C₄F₆ and C₄F₈. For C₄F₆/Ar plasmas, the measured ion current density was slightly higher than that obtained with C₄F₈/Ar.

B. Infrared laser absorption spectra for C₄F₆-based discharges

Figures 3–5 show the densities of CF, CF₂, and COF₂ calculated from the absorption spectra obtained with C₄F₆ and C₄F₈/Ar plasmas at 40 sccm gas flow for pressures of 6 and 20 mTorr, and 600 W inductive power. The radical density data were obtained during fluorocarbon deposition (no rf bias, Fig. 3), fluorocarbon etching (an rf bias producing a self-bias voltage of ~100 V was applied and resulted in fluorocarbon etching, Fig. 4), and Si etching (also at ~100 V self-bias voltage, Fig. 5). The measurement during etching of fluorocarbon films was performed after a deposition experiment without bias. Overall, the densities of CF, CF₂, and COF₂ decrease with increasing Ar percentage. The CF₂ partial pressure is about 50 times greater than that of CF at 20 mTorr. The CF species density is higher for pure C₄F₆ and 20% Ar/C₄F₆ plasmas at 6 mTorr than at 20 mTorr during fluorocarbon deposition conditions. On the other hand, the CF density is higher for pure C₄F₆ plasmas at 20 mTorr than at 6 mTorr during fluorocarbon and Si etching. The CF density is very similar at higher percentages of added Ar at both 6 and 20 mTorr during fluorocarbon deposition and etching. The densities of CF₂ and COF₂ species are higher at 20 mTorr than at 6 mTorr for a given gas feed mixture. The COF₂ is produced in pure fluorocarbon plasma with or without Ar from the reactor window effect.

The comparison of C₄F₆/Ar and C₄F₆/O₂ discharges will be discussed next. Figure 6 shows the densities of CF, CF₂, and COF₂ calculated from the absorption spectra obtained with C₄F₆/O₂ and C₄F₆/Ar plasmas at 40 sccm gas flow, 20 mTorr pressure, and 600 W inductive power. Again, the radical density data were obtained during fluorocarbon deposition (no rf bias, Fig. 6). Very similar results as shown in Fig. 6 were obtained during fluorocarbon and Si etching, but are not shown for the sake of brevity. The CF density is higher for C₄F₆/Ar plasmas than for C₄F₆/O₂ for all of the above processes. The CF₂ density is comparable for both C₄F₆/Ar and C₄F₆/O₂ plasmas, except at 40% gas additive, where a systematic difference seems to be indicated in all
data, i.e., the CF₂ density is higher for C₄F₆/40% Ar plasmas than for C₄F₆/40% O₂. Both the CF and CF₂ partial pressures decrease monotonically as the amount of O₂ and Ar are increased. The density of COF₂ is higher for C₄F₆/O₂ than for C₄F₆/Ar and reaches a maximum at 60% O₂ additive.

Figure 7 shows a comparison of the densities of CF, CF₂, and COF₂ calculated from the absorption spectra obtained with C₄F₆/Ar and C₄F₈/Ar plasmas operated at 40 sccm gas flow, 20 mTorr pressure, and 600 W inductive power. It shows that CF and COF₂ for C₄F₈/Ar plasmas contribute a higher percentage of the total pressure than for C₄F₆/Ar and reaches a maximum at 60% O₂ additive.

Figure 7 shows a comparison of the densities of CF, CF₂, and COF₂ calculated from the absorption spectra obtained with C₄F₆/Ar and C₄F₈/Ar plasmas operated at 40 sccm gas flow, 20 mTorr pressure, and 600 W inductive power. It shows that CF and COF₂ for C₄F₈/Ar plasmas contribute a higher percentage of the total pressure than for C₄F₆/Ar and reaches a maximum at 60% O₂ additive.

C. Fluorocarbon deposition and etching data

In fluorocarbon gas plasmas, fluorocarbon film deposition occurs along with fluorocarbon etching. In Figs. 8(a) and 8(b), fluorocarbon deposition rates obtained without rf bias and fluorocarbon etching rates at −100 V self-bias voltage are shown, respectively. The data are plotted as a function of feed gas composition for both C₄F₆/Ar and C₄F₈/Ar. For the pure fluorocarbon gases, the deposition rate using C₄F₆ is about 40% higher than for C₄F₈ at the conditions used here (600 W source power, 20 mTorr pressure). We observe an overall trend towards lower fluorocarbon deposition rates as Ar is added to both C₄F₆ and C₄F₈. This may be expected because of the reduced flow of fluorocarbon molecules into the reactor as an increasing proportion of Ar is added to the C₄F₆/Ar and C₄F₈/Ar gas mixtures (total flow fixed at 40 sccm). For most gas compositions, the deposition rate is higher for C₄F₆/Ar than for C₄F₈/Ar, except for 80% Ar and higher, where the deposition rates become very similar.

Figure 8(b) shows the corresponding fluorocarbon etching rate at −100 V self-bias voltage. The etching rate measured for pure C₄F₈ is more than twice the etching rate measured for pure C₄F₆. The etching rates for both fluorocarbon gases increase up to 70% Ar additive, and above that quickly decrease for both gas mixtures. At all gas compositions examined here the fluorocarbon etching rate is higher for C₄F₆/Ar than for C₄F₈/Ar. Overall higher fluorocarbon deposition rate and lower fluorocarbon etching rate are observed for C₄F₆ than for C₄F₈.

D. Effects of adding Ar to C₄F₈ and C₄F₆ on SiO₂ and Si etching

1. SiO₂ etching behavior as a function of rf bias

Figure 9 shows the behavior of the SiO₂ etching rate as a function of rf self-bias voltage for pure C₄F₈ and C₄F₆. The
curves shown in Fig. 9 exhibit the familiar behavior of the SiO$_2$ etch rate as a function of rf bias power in high-density fluorocarbon plasmas. We conclude from Fig. 9 that the zero bias fluorocarbon deposition rate and the etching threshold rf bias voltage for C$_4$F$_6$ are higher than for C$_4$F$_8$. The SiO$_2$ etching rate is higher for C$_4$F$_8$ than obtained with C$_4$F$_6$ at the same rf bias power or at a given self-bias voltage.

The behavior shown in Fig. 9 is also representative of the qualitative variation of the etching rates of silicon and resist with rf bias. The absolute magnitude of the etching rate in the high-voltage regime varies strongly with material, reflecting differences in thickness of the fluorocarbon films that are present during steady-state etching on the surfaces of these materials.

2. Variation of the SiO$_2$ and Si etching rate with Ar content in C$_4$F$_6$/Ar and C$_4$F$_8$/Ar

The dependence of the SiO$_2$ etching rates at a fixed self-bias voltage of $-100$ V on gas composition in C$_4$F$_6$/Ar and C$_4$F$_8$/Ar gas mixtures is shown in Fig. 10(a). This etching condition is above the fluorocarbon suppression regime. The etching rates exhibit a similar behavior as a function of the Ar percentage in either C$_4$F$_6$/Ar or C$_4$F$_8$/Ar. The SiO$_2$ etching rates increase up to 60% Ar where they reach their highest level and then decrease as the Ar percentage is increased further. The etching rate is higher for C$_4$F$_6$/Ar than for C$_4$F$_8$/Ar, which may be attributed to the higher F/C ratio of the C$_4$F$_8$/Ar discharge. These data show that high rate SiO$_2$ etching is possible in both C$_4$F$_6$/Ar and C$_4$F$_8$/Ar discharges up to high Ar concentrations. When up to about 60% Ar is added to the fluorocarbon gases, the SiO$_2$ etching rate is apparently not limited by the reduced fluorocarbon gas flow.

Figure 10(b) shows the poly-silicon etching rate as a function of Ar percentage in C$_4$F$_6$/Ar and C$_4$F$_8$/Ar gas mixtures. Initially, for both C$_4$F$_6$/Ar and C$_4$F$_8$/Ar discharges a monotonic increase of the Si etching rates with increasing Ar percentage is seen. Above 60% gas additive, the Si etching rates decrease. As for SiO$_2$, the etching rate is higher for C$_4$F$_6$/Ar than for C$_4$F$_8$/Ar.

The SiO$_2$/Si etch rate ratio is shown in Fig. 10(c). The etching selectivity trends for both gas mixtures as a function of %Ar are similar to the behavior of the SiO$_2$ etch rates. The SiO$_2$/Si etching selectivity is slightly higher for C$_4$F$_6$/Ar discharges than for C$_4$F$_8$/Ar discharges. Adding Ar enables an increase of the SiO$_2$/Si etching selectivity for intermediate Ar concentrations for both C$_4$F$_6$/Ar and C$_4$F$_8$/Ar.

The etch yields of SiO$_2$ and Si samples in C$_4$F$_6$/Ar and C$_4$F$_8$/Ar discharges are shown in Fig. 11. The etch yield reaches the highest level at 40% Ar and 60% Ar for SiO$_2$ and Si samples for C$_4$F$_8$ and C$_4$F$_6$/Ar gases, respectively. The etch yield value of C$_4$F$_8$/Ar plasma is higher than for
C$_4$F$_6$/Ar plasma because of the surface fluorination effect to be discussed below.

3. SiO$_2$/resist etching selectivity for C$_4$F$_6$ and C$_4$F$_8$ versus amount of added Ar

Adding Ar to C$_4$F$_6$ and C$_4$F$_8$ enables an increase of the SiO$_2$/resist etching selectivity. Figure 12 shows the resist etching rate as a function of gas composition. The etch rate trends are similar to those obtained when etching deposited fluorocarbon material. For both C$_4$F$_8$ and C$_4$F$_6$ gas mixtures, the etching rate increases sharply when the amount of Ar is increased above 40% Ar and goes through a maximum at 70% Ar. The resist etching rate decreases when more than 70% Ar was added. For all gas compositions, the resist etching rate is smaller for C$_4$F$_6$/Ar than for C$_4$F$_8$/Ar. Because of a slower SiO$_2$ etching rate in C$_4$F$_6$-rich gas mixtures, this does not result in higher SiO$_2$/resist etching selectivity for Ar-lean C$_4$F$_6$/Ar gas mixtures relative to C$_4$F$_8$/Ar. For intermediate Ar concentrations, the SiO$_2$/resist etching selectivity for C$_4$F$_6$/Ar becomes higher than that measured for C$_4$F$_8$/Ar.

E. Surface analysis data and discussion

To obtain information on changes of the surface chemistry as a result of adding Ar to C$_4$F$_8$ and C$_4$F$_6$ discharges, XPS analysis was performed with plasma etched polycrystalline silicon and SiO$_2$ samples processed in either pure C$_4$F$_8$ or C$_4$F$_6$, C$_4$F$_8$/20% Ar or C$_4$F$_6$/20% Ar, C$_4$F$_8$/40% Ar or C$_4$F$_6$/40% Ar, C$_4$F$_8$/60% Ar or C$_4$F$_6$/60% Ar, and C$_4$F$_8$/80% Ar or C$_4$F$_6$/80% Ar plasmas. The samples were processed with a self-bias voltage of −100 V at the gas compositions given above. Figures 13–15 show high resolution C(1s) electron emission spectra obtained after different plasma processes.

For the data of Fig. 13, a 300-nm-thick fluorocarbon layer was deposited on a Si sample in either a C$_4$F$_6$ or a C$_4$F$_8$
discharge. The deposited fluorocarbon film produced in C₄F₆ exhibits a higher CF₂ component than that for C₄F₈, and the overall C(1s) intensity is greater for C₄F₆ than for C₄F₈.

Comparative surface analysis results for the steady-state fluorocarbon film on a Si substrate under etching conditions for both C₄F₈/Ar and C₄F₆/Ar are shown in Fig. 14. These comparisons demonstrate that the CF₂ group is dominant for the fluorocarbon layer for films produced in the pure FC gases, similar to the results obtained with deposited fluorocarbon films. As Ar is added to both gases, the chemical components of the fluorocarbon film change. The effect of the Ar additive is clearly visible as a significant reduction in the fluorine content of the fluorocarbon layer. The CF₂ group decreases, and the Si–C group increases as Ar is added. At a low Ar proportion, the fluorocarbon film thickness is greater for C₄F₆ than for C₄F₈. At 80% Ar, the carbonaceous film consists mostly of Si–C type bonds for both gas mixtures, and the surface chemical components are almost the same for C₄F₆ and C₄F₈, as is the film thickness.

Corresponding results for a SiO₂ surface are shown in Fig. 15. For the pure fluorocarbon gas, a thicker fluorocarbon film was obtained using C₄F₆ than that for C₄F₈. We also observe the following difference when comparing the C(1s) data of Figs. 14 and 15: For a Si surface, the CF₂ group is dominant for both C₄F₆ and C₄F₈ (see Fig. 14). This is not the case for SiO₂, for which the C–CF₂ group has the highest intensity (see Fig. 15). In the case of C₄F₈, this observation appears consistent with our previous CF₂ gas phase density data measured by the IRLAS method. There we observed a significant reduction of the CF₂ partial pressure for an etching SiO₂ surface relative to a SiO₂ surface without rf bias (fluorocarbon film deposition) or a Si surface etching using identical conditions.

We also measured the thickness of the modified Si surface layer in real time using in situ ellipsometry, and compared these results with data obtained from analysis of the XPS.
spectra. We find that both ellipsometry and XPS lead to consistent results for the steady-state fluorocarbon film thickness, and these are displayed in Fig. 16. Figure 16 shows that C₄F₆/Ar produces thicker fluorocarbon layers on the Si surface than C₄F₈/Ar (up to 70% Ar). When 80% Ar was added, the steady-state fluorocarbon film thickness decreased for the C₄F₆/Ar gas mixture, whereas the film thickness for C₄F₈/80% Ar became greater.

The changes in Si and SiO₂ etching behavior with gas composition (see Fig. 10) may be expected to be mirrored in the behavior of the steady-state fluorocarbon film thickness that exists during etching on these surfaces. In addition, the SiO₂/Si etching selectivity should be related to this parameter. In Fig. 17 we compare the SiO₂ and Si etching yields as a function of steady-state FC film thickness. Figure 17 shows that thicker steady-state fluorocarbon films coincide with lower etch yields for both C₄F₈/Ar and C₄F₆/Ar gas mixtures. We also observe that for a given fluorocarbon film thickness, the etch yield measured for C₄F₈/Ar is greater than for C₄F₆/Ar.

Figure 18 shows the atomic density ratio of fluorine to carbon (F/C ratio) of the steady-state fluorocarbon layer during Si etching as a function of the Ar content. The F/C ratio was determined using methods described in Refs. 2 and 11. Figure 18 shows that the surface layer exhibits a higher F/C ratio during C₄F₈/Ar etching than during C₄F₆/Ar etching. This suggests that the F/C ratio of the fluorocarbon layer is to a significant extent determined by the nature of the fluorocarbon feedgas. In previous work it was concluded that for C₂F₆ and CHF₃ discharges SiO₂ is being etching by a direct
reactive ion etching mechanism, where the ions provide the chemical constituents necessary for etching. The SiO$_2$ etching yield was observed to increase roughly linearly with the average ion F/C ratio for C$_2$F$_6$ and CHF$_3$ gases for which the fluorocarbon surface layers were thin. For the present studies fairly thick fluorocarbon surface layers are produced on both SiO$_2$ and Si, and the etching rates of both SiO$_2$ and Si should be related to the F/C ratio of the fluorocarbon layer. This mechanism helps to explain why the SiO$_2$ etching rate is larger for C$_4$F$_8$/Ar than for C$_4$F$_6$/Ar.

The change of the fluorine content of the fluorocarbon films when adding Ar to the fluorocarbon gases is presumably related to the increased ion bombardment resulting from the higher plasma density of C$_4$F$_8$/Ar and C$_4$F$_6$/Ar discharges. For both C$_4$F$_6$ and C$_4$F$_8$, the F/C ratio decreases as the ion current density to the substrate increases. For both gases, the ion current density is 30% higher for C$_4$F$_6$.

Figure 20 shows the changes of the relative contribution of C–C, C–CF$_x$, CF, CF$_2$, and CF$_3$ species in the fluorocarbon surface layer as a function of ion current density measured for different proportions of Ar. The CF, CF$_2$, and CF$_3$ species percentage in the fluorocarbon layer decreases as the ion current increases (due to raising the amount of Ar in the fluorocarbon gases). A comparison of plots of these data versus percentage of Ar in C$_4$F$_6$/Ar or ion current density, respectively, showed that the ion current plays the dominant role in these surface chemistry changes. The behavior shown in Fig. 20 is nearly independent of the fluorocarbon gas and primarily determined by the magnitude of the ion current density. The trend of the CF and CF$_2$ species percentages in the fluorocarbon layer with ion current density increases with increasing Ar proportion. C–CF$_x$ intensity changes little with ion current for both gas mixtures, whereas the C–C intensity increases strongly when the ion current increases and the CF, CF$_2$, and CF$_3$ content of the fluorocarbon film is reduced.

IV. SUMMARY AND CONCLUSION

C$_4$F$_6$ discharges are significantly more polymerizing than C$_4$F$_8$ discharges, with many consequences, including lower SiO$_2$ etching rates for the pure fluorocarbon gas. Without gas additives it can become difficult to operate C$_4$F$_6$ discharges at certain conditions, e.g., high inductive power/high pressure, where excessive polymerization makes pressure control at a constant gas flow rate difficult. The increased polymer-
ization rates necessitate longer tool cleaning times for reproducible process conditions. On the other hand, adding Ar to C₄F₆ reduces the importance of these factors and enables SiO₂ etching processes with higher selectivity relative to resist and Si materials than using C₄F₈/Ar. The improved operating parameter range can be explained by a monotonic decrease of the gas phase density of CF and CF₂ radicals as the Ar proportion in Ar/C₄F₆ is increased.

Ellipsometry and XPS consistently showed that during steady-state etching the silicon surface is covered by a relatively thick fluorocarbon layer varying from 2 to 4 nm when the amount of Ar added to C₄F₆ and C₄F₈ was changed from 20% to 80%. A thicker, less fluorinated, fluorocarbon layer was obtained for C₄F₈/Ar than for C₄F₆/Ar. The fluorine content of the steady-state fluorocarbon layer dramatically decreased as the amount of Ar in the discharges was increased. For a given thickness of the steady-state fluorocarbon film on silicon and SiO₂, higher etching rates were measured for C₄F₈/Ar than for C₄F₆/Ar. These observations provide an explanation for the improved SiO₂/Si etching selectivity seen for Ar-rich Ar/C₄F₆ gas mixtures.

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Fig. 20. Relative contribution (in percent) of C–C, C–CFₓ, CF, CF₂, and CF₃ to the C 1s spectra of the steady-state fluorocarbon surface layer shown in Fig. 7 as a function of ion current density. The samples were processed at 600 W inductive power, 20 mTorr pressure, 40 sccm gas flow, and −100 V self-bias voltage.