Role of Surface Temperature in Fluorocarbon Plasma-Surface Interactions


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Role of surface temperature in fluorocarbon plasma-surface interactions

Caleb T. Nelson, Lawrence J. Overzet, and Matthew J. Goeckner
Department of Electrical Engineering, University of Texas at Dallas, PO Box 830688, Richardson, TX 75083
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This article examines plasma-surface reaction channels and the effect of surface temperature on the magnitude of those channels. Neutral species CF4, C2F6, and C3F8 are produced on surfaces. The magnitude of the production channel increases with surface temperature for all species, but favors higher mass species as the temperature is elevated. Additionally, the production rate of CF2 increases by a factor of 5 as the surface temperature is raised from 25°C to 200°C. Fluorine density, on the other hand, does not change as a function of either surface temperature or position outside of the plasma glow. This indicates that fluorine addition in the gas-phase is not a dominant reaction. Heating reactors can result in higher densities of depositing radical species, resulting in increased deposition rates on cooled substrates. Finally, the sticking probability of the depositing free radical species does not change as a function of surface temperature. Instead, the surface temperature acts together with an etchant species (possibly fluorine) to elevate desorption rates on that surface at temperatures lower than those required for unassisted thermal desorption. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4729445]

I. INTRODUCTION

The role of surface interactions in plasmas has been a topic of much discussion over the past decade. These interactions are difficult to model and predict on macroscopic scales because of the vast number of variables affecting surface conditions and the complexity of the surface feedback into the plasma. However, the effect of surface temperature is extremely important in processing plasmas. Cryogenic temperatures have been used as an alternative to the Bosch process in deep silicon etching. Elevated surface temperatures can be used to limit polymer deposition on chamber walls, as well as to change etch selectivity for common surfaces. Nonetheless, many reactors only control the temperature of a few surfaces, effectively allowing the remaining surfaces to be heated by the plasma. This can produce severe hysteresis in the results causing significant process shift and potentially creating changing film morphology and surface features. Thus, it is important to understand how surface temperature plays a role in changing both the surface material and, through feedback processes, the plasma.

A few researchers have examined changes in surface interactions as functions of wall temperature. Ito et al. observed an increase in CF2 and CF3 densities of 2 to 3 orders of magnitude in CF4 plasmas with wall temperatures of 200°C versus 50°C. They offered two possible explanations: (1) decreased loss to the walls or (2) increased dissociation of vibrationally excited CF4. Zhou et al. examined the influence of wall temperature in CF4 plasmas. They concluded that there is little effect below 50°C. Above this temperature, reduced losses of CF2 and CF3 were thought to increase respective densities in the plasma. In contrast to these conclusions, Doh and Horike examined radical fluxes near a temperature controlled platen in a CF4 plasma through mass spectroscopy. They also found that the densities of CF, CF2, and CF3 increased as the temperature of the platen increased, with CF3 showing the greatest enhancement. However, each of these densities was greatest near the surface, suggesting the dominance of a surface-driven production rate that increases with temperature. Finally, Hirashita et al. have looked separately at the isolated effects of surface temperature (no plasma) and argon ion bombardment on fluorocarbon films. They demonstrated that both temperature and ion induced desorption processes preferentially reduce the F/C ratio of the film. Above 200°C, CF, CF2, and CF3 bonds in the film are reduced while the percentage of C-CFx bonds increases. Ion dosages ranging from 2 to 6 × 1012 Ar+/cm2 were found to promote surface changes similar to temperatures ranging from 300 to 500°C.

Each of these studies shares the common observation that the densities of small CF3 radicals increase as the wall temperature increases. However, explanations for this phenomenon vary, and it has been difficult to explain the dominant deposition mechanisms. Because of this difficulty, the effect of surface temperature on the sticking coefficients of common fluorocarbon species has not been identified. Surface temperature alone does not cause significant desorption below 200°C, but ion and radical fluxes to the surface enhance the effect of surface temperature causing significant changes in both the plasma and the surface conditions. Species with high loss rates either on the walls or through addition reactions in the gas-phase will have significantly reduced densities as the distance from the plasma source is increased. For this reason, it is important to understand surface temperature not only as an isolated effect, but also as a function of the surface proximity to the plasma.

It is the purpose of this paper to discuss the regulation of surface interactions through understanding reaction channels on the surface and how they are affected by surface conditions. Primarily two specific surface conditions will be discussed. The relative fluxes of species at the surface

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4Electronic mail: goeckner@utdallas.edu
vary with proximity to the plasma. Surface temperature can alter the effect of those species. Species with large losses either in the bulk or on the surface should decrease significantly as a function of distance from the plasma source. In order to examine these effects, this paper will first provide a description of the reactor and the conditions used in the experiment. The densities of semistable radicals measured by FTIR will then be analyzed in order to examine potential changes in gain and loss rates for the radical species with increasing wall temperature. Local measurements of fluoro- and ion fluxes to the surface of interest will also be discussed. Finally, surface deposition rates will be examined both as functions of wall temperature (through feedback to the plasma) and chuck temperature (direct effect of temperature) before examining possible explanations for the results.

II. EXPERIMENT

The modified gaseous electronics conference (mGEC) reference cell was used in this study to examine plasma-wall interactions. As seen in Fig. 1, the specialized reactor differs from the standard GEC cell in the ability to allow flexible chamber diameters (20, 40, and 60 cm) through the use of interchangeable 1/2 in thick aluminum cylinders. In the following experiments only the 60 cm diameter wall is used. The five-turn inductive source sits in an aluminum bucket with a 12.7 cm diameter alumina window. A transmitted inductive power of 400 W at 13.56 MHz is coupled into the plasma through a conventional L-type matching network. The inductive source can be displaced on its vertical axis, providing a range (hereafter referred to as the electrode gap) of 3 cm to 17 cm. Steady-state measurements were taken at residence time of 7 s was obtained, exacerbating the effect of plasma-wall interactions.

A constant pressure of 30 mTorr was used throughout the experiments. A total flow rate of 33 sccm was set, with 30 sccm coming from a c-C4F8 source, while the remaining 3 sccm was devoted to an argon flow in order to perform actinometry measurements. Under these conditions a chamber residence time of 7 s was obtained, exacerbating the effect of plasma-wall interactions.

A number of diagnostics were used to measure radical and ion densities in the plasma. A Wise probe was used to measure ion fluxes. The probe allows accurate measurements in spite of the polymer buildup on the probe because the 50 kHz signal can be transmitted through the insulating layer. The probe was placed 2 cm above the lower electrode in the center of the chamber. Measurements of ion densities are used to provide an estimate of the ion flux to the chuck surface.

Fluorine density was measured via actinometry. Here, argon was used as 10% of the total feedgas to act as an actinometer. Fluorine density was obtained using Eq. (1), where \( I_F \) is the intensity of the fluorine transition at 703.7 nm, \( I_{Ar} \) is the intensity of the argon transition at 750.4 nm, and \( C_{F,Ar} \) is a correction factor accounting for the relative excitation cross-sections. Here \( C_{F,Ar} \) is estimated to be 0.6

\[
N_F = C_{F,Ar} \frac{I_F}{I_{Ar}}.
\]

The densities of larger radical species, \( C_{x,F,y} \), were measured using FTIR spectroscopy. As seen in Fig. 2, the IR beam was passed through the chamber multiple times (4–24) using a White cell to increase signal-to-noise ratio. The number of passes was chosen to maximize the signal, while avoiding saturation of the MCT-A detector. The FTIR beam path filled the area 1 to 5 cm above the chuck. It is important to note that all diagnostic measurements remained stationary relative to the chuck surface, while the inductively coupled plasma source coil was raised and lowered to change the electrode gap. Steady-state measurements were taken at 0.5 cm resolution and averaged across 64 scans. Absolute densities for each species were obtained by subtracting temperature fitted spectra for each species according to the method outlined by Nelson et al.
Finally, a Jobin-Yvon ellipsometer fixed at 633 nm was used to measure deposition and etch rates on a 1 cm² Si sample placed on top of the chuck. Thermal paste was applied to the back of the sample in order to ensure a uniform surface temperature. Measured deposition rates were compared to ex situ multiwavelength (250–750 nm) scans in order to double check accuracy.

III. RESULTS AND ANALYSIS

A generic process rate model can be used to understand interactions between plasma species and surfaces. A number of researchers have used site-balance equations to model process rates as functions of fluxes to the surface. Equation (2) represents a formalized version of these models presented by Sant et al.¹⁵

\[
\text{Process rate} = \left[ \sum_{\text{deposit}} \frac{K_{\text{ion}}}{\rho_{\text{film}}} (\Gamma_{\text{ion}}) S C_{\text{ion}} + \sum_{\text{deposit}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} (\Gamma_{\text{rad}}) S C_{\text{rad}} \right] - \left[ \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} (\Gamma_{\text{ion}}) Y_{\text{ion,film}} - \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} (\Gamma_{\text{rad}}) Y_{\text{rad,film}} - \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{sub}}} (\Gamma_{\text{ion}}) Y_{\text{ion,sub}} - \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{sub}}} (\Gamma_{\text{rad}}) Y_{\text{rad,sub}} \right] / C_0.
\]  

In Eq. (2) \( K \) is a proportionality constant accounting for the number of atoms in the incoming molecule, \( \rho \) is the density of the C\(_x\)F\(_y\) film or the substrate, \( \Gamma \) is the flux of particles to the surface, \( SC \) is the probability of the particle bonding to the surface, while \( Y \) is the etch yield, or number of particles removed from the surface per impinging molecule. Each reaction represented in Eq. (2) has a probability that is a function of the density of open-bond sites on the surface, the surface temperature, the energy of the incoming particle, the angle of impact, and the structure of the surface and the incoming particle.

As seen in the model, both ions and radicals have the ability to interact with surfaces in the reactor. These can be divided into species that etch the surface and those that deposit on the surface. Ions can contribute to film deposition both directly through covalent bonding and by creating surface sites as a catalyst for radical deposition. Alternately, they can contribute to surface etch through sputtering or through breaking surface bonds to allow for the production of volatile byproducts at the surface. In fluorocarbon plasmas, atomic and molecular fluorine are likely responsible for chemical etching. Meanwhile, carbon containing free-radicals (CF, CF\(_2\), CF\(_3\), C\(_2\)F\(_3\), etc.) and unsaturated radicals (C\(_2\)F\(_4\), C\(_3\)F\(_6\), etc.) could either contribute to film growth or be produced as a result of film etching. Finally, stable neutral species (CF\(_x\), C\(_2\)F\(_6\), C\(_3\)F\(_8\), etc.) are unlikely to be reactants at the surface, but could likely be etch products.

In order to discuss the effects of surface proximity and temperature, the gas-phase components will be examined first. The densities of species with measurable FTIR spectra (C\(_2\)F\(_8\), C\(_2\)F\(_6\), CF\(_4\), C\(_3\)F\(_8\), C\(_2\)F\(_4\), and CF\(_2\)) are investigated both as functions of the electrode gap and wall temperature. These densities can be used to estimate quantitative magnitudes for the gain and loss channels of each species, allowing a direct observation of the effect of surface temperature. This discussion will be followed by point measurements of fluorine density as a function of electrode gap and surface temperature. Ion fluxes will be analyzed under the same conditions.
conditions to determine their predominant interaction with the surface. Finally, the interpreted gas-phase data will be used in understanding the factors that control the changes in deposition rate with proximity and temperature.

A. Stable species

Although it is unlikely that the stable and metastable species capable of being measured by the FTIR are directly responsible for the majority of the deposition and etch occurring in the system, analysis of their gain and loss characteristics can provide some insight into the mechanisms controlling surface changes. In order to show the effects of both surface proximity and temperature, the first part of the discussion will focus on variations in the density of each species as functions of the electrode gap. We will then proceed by examining density changes at a fixed 16 cm electrode gap that are solely due to the effect of increasing wall temperatures.

1. Effect of electrode gap on species densities

Figure 3 shows the changes in the measured density of neutral species as a function of electrode gap. Only c-C₄F₈, C₂F₄, C₂F₆, and CF₄ are shown because of increasing noise in the measurement as the gap is decreased. A couple of observations stand out. First, as the electrode gap is decreased from 16 to 8 cm the density of each of the species drops, but the relative gas composition remains approximately constant. This indicates that the primary cause for the drop in density is due to an increase in the gas temperature in the FTIR beam. A secondary cause for this decay could be due to a large loss rate near the source, where the electron density and temperature are the largest. As the gap becomes smaller, this source region comes closer to the location where the species densities are being measured, and as a result, the loss rate is expected to increase.

The average gas temperature in the FTIR beam path when the electrode gap is 16 cm can be roughly calculated according to Eq. (3), where \( \nu_{\text{max}} \) is the wavelength of the peak maximum of the C-F deformation band at 963 cm\(^{-1}\), characteristic of c-C₄F₈ IR absorption

\[
T = (-1.337\nu_{\text{max}} + 1305.6)^2.
\]  

Using this approximation, an average gas temperature in the FTIR beam of 357 K can be estimated. Unfortunately, increased noise at lower gaps does not allow this method to be used to calculate the gas temperature. However, a line-averaged gas temperature above the chuck can be estimated by assuming that the drop in density is entirely due to gas temperature. These results are plotted in Fig. 4. It is important to note that these are line-averaged temperatures, primarily measured outside of the high-density region of the plasma. This means that gas temperatures in the high-density portion of the discharge will be significantly higher.

The second important observation of the change in densities with gap relates to the large variation in the relative gas composition that occurs below 8 cm. A couple of possibilities could explain this phenomenon. A sharp increase in electron density at these gaps could account for the decrease in c-C₄F₈ relative to other species in the gas-phase. Alternatively, the proximity of the cooled chuck could lower the total gas-temperature in the volume with high electron density, leading to increased breakdown of c-C₄F₈. Although, the authors were unable to ascertain the primary cause for this change, similarly large changes are seen in fluorine densities, ion fluxes, and deposition rates at small electrode gaps, indicating the importance of this step change in source proximity.

2. Effect of wall temperature on species densities

The second part of the experiment examines the effects of wall temperature on neutral species. The total gas density, \( n_{\text{Total}} \), in the FTIR beam path can be estimated using...
the ideal gas-law, and the line-average temperature can then be calculated with Eq. (3). Figure 5 shows that at 16 cm, thermal diffusion dominates the gas temperature directly above the chuck. In order to obtain a line-averaged temperature of 84 °C when the reactor walls are held at room temperature, we estimate that the gas temperature near the chuck is greater than 200 °C. This is because there must be a significant gradient in the gas temperature from the source region near the chuck to the room temperature walls. The source region is at least 1/4 the length of the FTIR beam, so the gas temperature near the chuck must be approximately four times higher than the average value measured.

This observation is important for two reasons. First, it suggests that within the range of wall temperatures examined, the temperature (and by correlation, the surface-flux) of particles in the FTIR beam path is primarily driven by heating from the plasma instead of the heating from the walls. This conclusion can be reached by comparing the gas temperature above the chuck with the walls held at room temperature. This situation is only exacerbated as the electrode gap is decreased. The gas temperature in the plasma region is always greater than the gas temperature in the ballast region. Second, the line-averaged temperature is used in Fig. 6 to plot the mole percentage (defined as \( n_CFC_2 / n_{total} \)) as a function of wall temperature, where the values have been normalized to the room temperature condition. The figure shows that as the wall temperature is raised, the relative gas composition contains less \( c-C_4F_8 \) and \( C_2F_4 \), and significantly more \( CF_2 \), \( C_2F_6 \), and \( C_3F_8 \). The reason behind these changes can be understood by analyzing the gain and loss processes for each of these species.

3. \( c-C_4F_8 \)

The easiest species to analyze is the source gas. Gains can be limited to flow rate into the chamber, while losses can be confined to electron impact dissociation and the pump.16 Gain and loss rates for \( c-C_4F_8 \) can be calculated as

\[
G_{\text{feed gas}} - L_{\text{elect}} - L_{\text{pump}} = Q - n_{C_4F_8} \left( \frac{T_{\text{ballast}}}{T_{\text{plasma}}} V_{\text{plasma}} k_{C_4F_8} + \frac{V_{\text{chamber}}}{t_{\text{res}}} \right) = 0.
\]

Here, \( Q \) is the flow rate of the feed gas, \( n_{C_4F_8} \) is the line averaged \( c-C_4F_8 \) density in the ballast region, \( V_{\text{plasma}} \) is the plasma volume, \( V_{\text{chamber}} \) is the chamber volume, \( n_e \) is the electron density, \( T_{\text{ballast}} \) is the gas temperature in the ballast region, \( T_{\text{plasma}} \) is the gas temperature in the plasma, and \( k_{C_4F_8} \) is the integrated total dissociation cross-section. The gain rate, \( G_{\text{feed gas}} \), is calculated from the rate of gas flowing into the chamber. Pump loss, \( L_{\text{pump}} \), can then be determined by the product of the measured \( c-C_4F_8 \) density and the chamber volume, divided by the residence time. The electron loss rate is then simply the difference between the gain from the feed gas and the loss to the pump.

The gain and loss rates plotted in Fig. 7 show that the total loss to electron impact dissociation reactions does not change as a function of temperature. However, as seen in the term \( L_{\text{elect}} / n_{C_4F_8} \), the product \( (T_{\text{ballast}} / T_{\text{plasma}}) V_{\text{plasma}} k_{C_4F_8} n_e \) is increasing as the wall temperature increases. The observed increase is not unexpected because the temperature of the gas in the source region is expected to be high (some\(^{17} \) have estimated it to be 800 K) and therefore should not be significantly affected by wall temperatures between 298 K and 472 K, since \( T_{\text{plasma}} > T_{\text{ballast}} \). The gas temperature in the ballast region will be controlled predominantly by the wall temperature, effectively increasing the product \( (T_{\text{ballast}} / T_{\text{plasma}}) V_{\text{plasma}} k_{C_4F_8} n_e \). The observed increase shows that for the wall temperature range studied, the only changes that should affect gas densities are gains and losses that occur on the walls or in the ballast region.
4. CF₄, C₂F₆, and C₃F₈

The primary benefit of this analysis is the ability to use the electron impact loss rate of c-C₄F₈ to predict the electron impact loss rates of other stable species. Using the logic presented by Nelson et al.,¹³ losses to electrons for other saturated radicals can be estimated as

\[ L_{\text{elect}} = \frac{L_{\text{elect,c-C₄F₈}}}{n_{\text{c-C₄F₈}}} \cdot \frac{k_{\text{c-C₄F₈}}}{k_{\text{C₅F₈}}} \cdot \frac{n_{\text{C₅F₈}}}{n_{\text{C₄F₈}}} \]  

(5)

The approximated loss rates can then be combined with losses to the pump, to assess net gain rates for each species by solving the continuity equation

\[ G_{\text{net}} - L_{\text{pump}} - L_{\text{elect}} = 0. \]  

(6)

The gain and loss rates for CF₄, C₂F₆, and C₃F₈ in molecules/s are provided in Fig. 8. The most recognizable feature in these plots is the increase in the net gain rate of each species as the wall temperature increases. Comparing the gain rates in Fig. 9 shows that as the wall temperature increases, the average mass of species coming off of the walls also increases. Alternately, it is possible that as the gas temperature increases, the rate coefficient for neutral-neutral recombination reactions could increase. However, this patch is less likely as the results provided in Sec. III D show that the increased surface temperature corresponds to an increase in desorption off of the surface.

A number of researchers have speculated about what occurs at the wall as the surface temperature increases. Hirashita et al.¹⁸ have investigated separately the effects of increased surface temperature and ion bombardment on fluorocarbon films. They found that as the surface temperature is raised above 200°C, the fluorine content of the film is reduced, while the number of C-C and C-F bonds in the film increases. That change is consistent with our finding of an increase in the gains of higher mass species. As the fluorine content in the film decreases, the production of stable species from the film surface will gravitate toward longer chain-lengths to reflect the lower F/C ratio.

5. CF₂ and C₂F₄

Gain and loss mechanisms for CF₂ can be similarly analyzed. A modified continuity equation is presented

\[ \frac{d[CF₂]}{dt} = G_{\text{elect}} + G_{\text{leftover}} - L_{\text{elect}} - L_{\text{pump}} - L_{\text{C₂F₄}}. \]  

(7)

Here, \( G_{\text{elect}} \) is estimated as primarily coming from the electron impact dissociation of C₂F₄. The loss to electron impact dissociation, \( L_{\text{elect}} \), and loss to the pump, \( L_{\text{pump}} \), are calculated as previously. Nelson et al.¹³ determined that the primary gas-phase loss of CF₂ in a large volume chamber is due to gas-phase concatenation to form C₂F₄. The rate constant for \( L_{\text{C₂F₄}} \) was estimated at \( 1.8 \times 10^{-14} \) cm³/s. At steady-state, the remaining gains and losses can be combined

![Fig. 7](URL) (Color online) Gain and loss rates for c-C₄F₈ as functions of wall temperature.

![Fig. 8](URL) (Color online) Gain and loss rates CF₄, C₂F₆, and C₃F₈ as functions of wall temperature.

![Fig. 9](URL) (Color online) Normalized gain rates CF₄, C₂F₆, and C₃F₈ as functions of wall temperature.
into a net gain, $G_{\text{leftover}}$. The magnitudes of these gain and loss processes are compared for 25 and 200 °C chamber walls in Fig. 10. Because the steady-state density of CF$_2$ increases by 60% with the hot chamber walls, losses increase correspondingly. However, there is not a corresponding increase in the gain rate from the electron impact dissociation of the plasma species. Figure 10 shows that even with large error bars, the leftover gain rate of CF$_2$ increases by a factor of 5 when the chamber walls are heated to 200 °C. This observation requires a production source of CF$_2$ at the wall that is magnified with elevated surface temperatures. This conclusion fits well with previous experiments involving purely thermal desorption. CF$_2$ is a metastable species, allowing it to desorb from the surface easily. Additionally, the CF$_2$ unit forms the backbone of carbon chains in the film. It is not surprising that as surface temperature increases, more of these bonds are severed.

The final species that could be accurately measured was C$_2$F$_4$. Measurable gain and loss processes can be summarized

$$\frac{d[C_2F_4]}{dt} = G_{\text{elect}} + G_{\text{CF}_2} - L_{\text{elect}} - L_{\text{pump}} - L_{\text{leftover}}. \quad (8)$$

Here, $G_{\text{elect}}$ is assumed to come primarily from the electron impact dissociation of c-C$_2$F$_8$. The term $G_{\text{CF}_2}$, represents gain from the gas-phase addition of CF$_2$ using the aforementioned rate constant. The loss to electron impact dissociation, $L_{\text{elect}}$, and loss to the pump, $L_{\text{pump}}$, are calculated as previously. At steady-state, all of the remaining gain and loss processes can be combined into a net loss term, $L_{\text{leftover}}$. The magnitude of these processes, measured at 25 and 200 °C wall temperatures, is plotted in Fig. 11. The only calculated term, which appears to change significantly, is the gain from CF$_2$ additions. With the increased density of CF$_2$, the gain from gas-phase additions becomes a significant gain mechanism, equivalent in magnitude to the gains from electron impact dissociation of c-C$_2$F$_8$. This is an important observation, as this gain channel is often neglected as trivial. The increase in gain must be balanced by an increased loss term. Neither the loss to electron impact dissociation nor the loss to the pump account for this increase. Several possibilities exist to explain the estimated 30% increase in leftover loss. First,

**B. Fluorine**

Fluorine is considered separately from the other species for two reasons. First, it is measured differently. The actinometry measurement is a point measurement and therefore difficult to compare to the line averaged measurements made by the FTIR. Second, in contrast to the semistable species discussed above, fluorine is a vigorous etchant, as seen in Eq. (2). This can occur either directly through a pure chemical etch or with the assistance of energetic ions. As evidenced by Eq. (1), actinometry measurements can be compromised both by the variation in the relative cross-sections for the actinometer and the gas being measured, as well as by the knowledge of the absolute density of the actinometer at the measurement location. Relative densities can be easily obtained as long as neither of these parameters is significantly affected. Local gas temperature can play a large role in the density of the actinometer. Measurements were made with 1 mm spot size focused along the chuck surface. For large gaps (8–16 cm), the line-averaged gas temperatures plotted in Fig. 4 allow the assumption that the gas temperature 1 mm above the chuck will be dominated by and approximately equal to the surface temperature. However, because the high-density region of the discharge appears to have a major impact on the local temperature, this assumption might not be valid for lower gaps. For this reason, only the ratio of intensities ($I_F/I_{Ar}$) is plotted for low gaps in Fig. 12. For larger gaps, argon density is calculated with the ideal gas law.

For large gaps (8–16 cm), the fluorine density near the chuck surface does not change as a function of the electrode separation. We expect fluorine to be primarily produced through electron impact dissociation of higher order
species.19,20 Both the electron density and temperature are highest near the source, falling off by factors of 10 and 2, respectively, 4 to 6 cm below the source. Thus, the dominant gain location for fluorine should be near the source coil, while it is lost in the bulk and on walls. However, the fact that the density near the chuck does not change significantly for 8 to 16 cm gaps indicates that the loss times in the bulk and on the chuck surface must be shorter than the diffusion time for fluorine. Using an upper estimate of 600 K for the gas temperature in this downstream region, a diffusion time can be estimated as

$$\tau_D = \frac{\Lambda_o}{D_F} \approx 1.5 \text{ ms},$$

where

$$D_F = \frac{\pi}{8} \bar{v}.\$$

Here, the characteristic length, $\Lambda_o$, is set to 8 cm and $D_F$ is the diffusivity of fluorine in the background gas, which is dependent on the mean free path, $\lambda$, and the collision frequency, $\bar{v}$. To compare this number, we will look at an estimated loss time for fluorine in

$$\text{F} + \text{CF}_2 \rightarrow \text{CF}_3. \quad (10)$$

The CF$_2$ density measured with room temperature walls is $6.75 \times 10^{13} \text{ cm}^{-3}$. A rate coefficient of $1.3 \times 10^{-11} \text{ cm}^3/\text{s}$, derived using data from Plumb and Ryan,21 is frequently used in modeling papers.19,22 These values provide an estimated loss time of 1.1 ms for the reactants. Equation (10) is only one of many possible loss processes for fluorine through addition reactions. However, the comparison of the loss time in Eq. (10) to the diffusion time for fluorine shows that the rate coefficients used for these reactions are too large. In order for the fluorine density to remain constant in the downstream region, the total loss time for all addition reactions must be much less than the diffusion time. Thus, either fluorine addition reactions occur at slower rates than currently modeled values, or the addition reactions are only efficient on surfaces with high ion bombardment (near the source).

Below an 8 cm electrode gap, $I_F/I_{Ar}$ increases as the gap is lowered. However, the density measurement is complicated by the possibility of changing argon densities as a function of gap. Lower gaps could have increased gas temperature in the measurement region and as a result, decreased argon density. Thus, the increase in F/Ar ratio at lower gaps could overestimate an increase in the absolute F density in the plasma. The intensity ratio increases by a factor of approximately 5, however, and it is very unlikely that the gas temperature 1 mm from the chuck surface rises by a similar factor (from 25 to 1200 °C). As a consequence, it is clear that the F density must be still increasing substantially.

Figure 12 also shows that the F density remains approximately constant as the wall (and chuck) temperature is changed. This phenomenon has been observed previously.3 However, no explanations have been offered. This result indicates that either (a) the gain and loss rates of F on the wall are not affected by surface temperature, (b) the ratio of the gain and loss rates of F on the wall are constant with surface temperature, or (c) the wall is not the dominant channel for gain and loss processes of F. The first conclusion does not fit with current or previous results. The production rate of neutral species (CF$_4$, C$_2$F$_6$, and C$_3$F$_8$), which consume free fluorine, all increase with wall temperature. Alternatively, if another loss channel, such as electron attachment dominates the loss of fluorine, then the density could remain approximately constant with wall temperature.

C. Ion flux

Ions play a major role in both deposition and etching processes in fluorocarbon plasmas.23 As previously discussed, low energy ions can affect the surface in a number of ways. They can be directly incorporated into the film after being neutralized on the surface. Ions also contribute to deposition processes by breaking surface sites, creating dangling bonds necessary for some neutral species to deposit. They contribute to the etching processes by sputtering molecules from the surface, as well as acting as a catalyst for chemical etching processes by breaking carbon-carbon bonds and allowing the creation of carbon-fluorine bonds.

Two significant trends stand out in the measurement of ion flux to the chuck surface in Fig. 13. First, as a function of electrode gap, the ion flux decreases by more than a factor of 20 as the source is pulled away from the chuck. The most significant portion of this decrease takes place between 4 and 8 cm electrode gaps. As mentioned previously, the plasma density within the measurement region appears to be decreasing in this range, accounting for the significant decrease in ion flux in this range. However, the ion flux continues to decrease by a factor of 4 as the electrode gap increases from 8 to 16 cm. The decrease can be attributed to losses to the walls and recombination.

The second observation is that the ion flux does not change significantly with the wall temperature, and by extension, the gas temperature. This is not surprising since the total power deposited into the discharge is kept constant; however, this trend necessitates that changes to the surface

![Figure 12](image-url)
as the temperature increases are only due to the direct affect of the surface temperature or through changing radical densities in the plasma bulk.

D. Deposition rates

The observations made about the gas-phase become significant when looking at what happens on the surface as a function of wall temperature. Deposition rates were measured on the chuck surface. In these measurements, the chuck temperature was altered independently from the wall temperatures. Gas-phase measurements were made to measure consistency during these experiments. For chuck temperatures between 20 and 220 °C, no change was observed in the gas-phase measurements. While the gas-phase chemistry was affected by the wall temperature, it was not affected by changes in the chuck temperature. The chuck surface is either too small or distant to independently affect the bulk plasma. This experimental result is fortuitous. It allows us to compare the surface measurements (film deposition/etch) at a given wall temperature to the gas-phase measurements (species causing film deposition and etch presented above) at the same wall temperature, knowing that there were no noticeable changes in the fluxes to the surface caused by changing the chuck temperature.

Figure 14 shows the measured deposition rate as the chuck temperature is increased. As expected, for all gaps and wall temperatures, the deposition rate decreases as the chuck surface temperature increases. This is not surprising, as the aforementioned increased desorption of CF₂, CF₄, C₂F₆, and C₃F₈ requires that the total deposition rate drops correspondingly. Perhaps more interesting is the relationship between the electrode gap and the chuck temperature. The deposition rate was measured at two electrode gaps (5 and 16 cm) as a function of chuck temperature. At the small gap (5 cm), the elevated chuck temperature transitions the deposition rate from large film growth to film etch, while at the large gap (16 cm) the temperature transition is much more mild and net etch is not achieved, even at high temperatures. We attribute this change largely to the increased presence of active species when the electrode gap is small. Both fluorine flux and ion flux to the chuck surface increase as the source is lowered. It is likely that depositing CₓFᵧ species act in a similar fashion. The increased fluxes allow the effect of surface temperature to be much more dramatic, while clearly showing that surface temperature must affect the sticking or etch yield coefficient of at least one of the active species.

Finally, two wall temperatures were used to measure the feedback effect through the plasma to the temperature controlled chuck. For both the 5 and 16 cm gaps, the deposition rate increased significantly when the wall temperatures were raised. However, as the chuck temperature increases, the difference in deposition rate for the two wall temperature conditions remained approximately constant. This can be seen by observing approximately constant gap between the 20 and 200 °C curves for the 5 cm gap and again for the 16 cm gap, respectively. The previous results showed that the fluorine flux and ion flux to the surface are unchanged by the wall temperature. Therefore, the change that is seen in the deposition rate on the chuck at any given chuck temperature as the wall temperature is increased from 20 to 200 °C cannot be due to either F radicals or ions! This means that the increase in deposition rate with increasing wall temperature can only be due to changes in the depositing neutral fluxes (CₓFᵧ) to the surface.

This conclusion can be used to further analyze the process rate at a single gap according to Eq. (2). Because no substrate etch occurs in our experiments, the last two terms can be removed from the equation. Additionally, no bias is applied to the chuck surface. Thus, the maximum ion energy is set by the plasma potential and is not dependent on the wall temperature. Previous measurements of the plasma potential in the mGEC yielded results between 20 and 30 V.14 With low ion energies, we do not expect a significant amount of sputtering. Thus, the process rate can be estimated as a function of surface temperature with three terms in

\[
\text{Process rate}(T) = \sum_{\text{deposit}} \frac{K_{\text{ion}}}{\rho_{\text{film}}} (\Gamma_{\text{ion}}) S_{\text{ion}}(T) + \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} (\Gamma_{\text{rad}}) S_{\text{rad}}(T) - \sum_{\text{etch}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} (\Gamma_{\text{rad}}) Y_{\text{film}}(T). \tag{11}
\]
For the purposes of simplicity, we will assume that fluorine is the major etchant species and that the film density does not change significantly in the range of temperatures being studied. Recognizing that neither the ion flux nor the fluorine flux to the surface change significantly, the difference in deposition rate at a 5 cm gap between the 20 and 200 °C wall conditions can be limited to a function of the neutral flux and their relevant sticking coefficients as

\[
\text{Process rate}_{200 \text{Walls}}(T) - \text{Process rate}_{20 \text{Walls}}(T) = \sum_{\text{deposit}} \frac{K_{\text{rad}}}{\rho_{\text{film}}} \left( \langle \Gamma_{\text{rad at 200 walls}} \rangle - \langle \Gamma_{\text{rad at 20 walls}} \rangle \right) = C, \tag{12}
\]

Figure 14 shows that the difference between the deposition rate with hot walls and cold walls at a 5 cm gap is approximately constant as the chuck temperature increases. Equation (12) proves that the constant offset at chuck temperatures below 200 °C can happen only if the sticking coefficient of the depositing neutrals is not surface temperature dependent. This means that the activation energy for the depositing neutrals is very close to 0. This result is consistent with what should be expected for heavy mass radical species being a primary deposition precursor at the chuck. The change in deposition rate between the hot wall and cold wall condition at a 16 cm gap does not appear to be quite constant. This could be due to a change in the dominant deposition precursor for locations far away from the source. Smaller radicals with lower sticking coefficients and higher activation energies will diffuse farther before being lost to the walls.

Because thermal desorption of these fluorocarbon films only begins around 200 °C, the effect of the surface temperature must be enhanced either by the ion or fluorine flux to the surface. We do not expect direct deposition from the ion flux to the surface or the ion-assisted component of the etch process (opening bond sites) to be highly temperature dependent. It seems likely, instead, that the decrease in deposition rate as the chuck surface temperature is elevated is dominated by the temperature dependence of the fluorine etch yield. This etching process is likely a combination of pure chemical etching and an ion-assisted etching process. These conclusions present a modified picture of the deposition and etch process in C4F8 plasmas. Here, the desorption rate of neutral species (CF2, CF4, C2F6, and C3F8) increases with surface temperature, but is controlled by fluorine availability and a temperature dependent reaction rate. As the temperature rises and the net desorption rate increases, the fluorine content of the film decreases, causing a relative increase in the desorption rate of heavier mass species. Meanwhile, the deposition rate due to radical species (possibly large free radicals) does not change significantly as a function of surface temperature. Overall these combined factors lead to a decrease in the net deposition rate on a surface as that surface temperature is raised. However, adjoining surfaces held to a lower temperature will have an increased deposition rate because of a larger density of available depositing free radical species.

IV. CONCLUSION

Through analyzing gas-phase and surface changes induced by surface temperature, a number of conclusions can be made. Fully saturated fluorocarbon species (CF4, C2F6, and C3F8) are likely produced at the surface. These production rates increase with the surface temperature. However, as the temperature is raised, production of heavier species (C4F8) is favored over lighter species (CF3). This is attributed to the changing nature of the film and the gas-phase. The film is expected to decrease in F/C ratio. Meanwhile, the preponderance of CF2 is gained from the surface at elevated temperatures, while fluorine densities remain the same. Gas-phase addition of fluorine to form neutral species seems unlikely because the fluorine density does not change significantly as a function of surface temperature. Therefore, fluoride density nor ion flux is found to change as a function of surface temperature. This allows us to conclude that increases in surface deposition on cooled surfaces compared to heated walls are due to an increase in depositing neutral fluxes. Although the depositing neutrals could not be measured (with the possible exception of C2F6), it is likely that higher mass free radicals are produced off of heated surfaces near the source and redeposited on the chuck. Finally, we observed that the sticking probability of the depositing radicals does not change significantly as a function of surface temperature. Instead, the decrease in deposition rates at elevated temperatures is due to an enhancement in the desorption rate controlled by the flux of an etchant species.

Further work in this area could include the use of a global model to compare the observations made in this article concerning plasma-surface interactions with the dominant predictions for gain and loss channels in current global models. Of particular interest is the refinement of coefficients for surface reactions such as those made by Kokkoris et al.19 A better understanding of these rate coefficients will lead to an increased usefulness of global models in predicting system changes for industrial plasmas.

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