

Optical emission spectroscopic studies and comparisons of CH_3F/CO_2 and CH_3F/O_2 inductively coupled plasmas

Qiaowei Lou, Sanbir Kaler, Vincent M. Donnelly,^{a)} and Demetre J. Economou^{b)} Plasma Processing Laboratory, Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204-4004

(Received 1 October 2014; accepted 2 December 2014; published 16 December 2014)

A CH₃F/CO₂ inductively coupled plasma (ICP), sustained in a compact plasma reactor, was investigated as a function of power (5-400 W) and feed gas composition, at a pressure of 10 mTorr, using optical emission spectroscopy and rare gas actinometry. Number densities of H, F, and O increased rapidly between 74% and 80% CO₂, ascribed to the transition from polymer-covered to polymer-free reactor walls, similar to that found previously in CH_3F/O_2 ICPs at 48% O₂. Below 40% O₂ or CO₂, relative emission intensity ratios were almost identical for most key species in CH₃F/O₂ and CH₃F/CO₂ ICPs except for higher OH/Xe (a qualitative measure of OH and H₂O densities) over the full range of CH_3F/O_2 composition. The number density of H, F, and O increased with power in CH₃F/CO₂ (20%/80%) plasmas (polymer-free walls), reaching 4.0, 0.34, and 1.6×10^{13} /cm³, respectively, at 300 W. The CO number density increased with power and was estimated, based on self-actinometry, to be 8.8×10^{13} /cm³ at 300 W. The CO₂ number density was independent of power below 40 W (where very little decomposition occurred), and then decreased rapidly with increasing power, reaching 2.8×10^{13} /cm³ at 300 W, corresponding to 83% dissociation. Films deposited on p-Si, 10 cm from the open, downstream end of the plasma reactor, were analyzed by x-ray photoelectron spectroscopy. Between 10% and 40% CO₂ or O₂ addition to CH₃F, film deposition rates fell and O content in the films increased. Faster deposition rates in CH₃F/CO₂ plasmas were ascribed mainly to a larger thermodynamic driving force to form solid carbon, compared with CH₃F/O₂ plasmas. Oxygen content in the films increased with increasing CO₂ or O₂ addition, but for the same deposition rate, no substantial differences were observed in the composition of the films. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4904213]

I. INTRODUCTION

Selective, anisotropic etching of silicon nitride (SiN_x) over Si or SiO₂ is important for fin field-effect transistor gate fabrication.¹⁻⁴ This process is carried out in hydrogencontaining fluorocarbon (CH_xF_v) plasmas such as CH₃F, with addition of O_2 .^{2,5–7} Recently, we reported a study of CH₃F/ O₂ discharges, sustained in a compact inductively coupled plasma (ICP) reactor.^{8–10} For equal CH₃F and O₂ feed gas flows, the H-atom density, derived from optical emission spectroscopy and rare gas actinometry, was 5.4×10^{13} cm⁻³ at 400 W, 10 mTorr, and a peak gas temperature of 900 K at the center of the discharge, indicating a high degree of dissociation of the CH₃F feedstock gas. For the same conditions, much lower F and O atom number densities $(8.3 \times 10^{12} \text{ and}$ $5.9 \times 10^{12} \text{ cm}^{-3}$, respectively) suggested that fluorine and oxygen are mostly contained in HF, CO, CO₂, H₂O, and OH. Using a self-actinometry method, the absolute CO number density was found to be 2.9×10^{13} /cm³ at 300 W, which is about half the oxygen fed into the reactor.¹⁰ An abrupt transition was found in the number densities of H, O and most notably, F as the O_2 percentage crossed 48%. This was explained by the competition between the deposition of a hydro-fluorocarbon film on the reactor walls, and the etching of that film by O-atoms. When the etching rate exceeded the deposition rate at >48% O₂, the reactor walls remained filmfree at steady-state, and the reaction of F atoms on the walls to form HF greatly slowed, causing the F number density to increase by a factor of 4. Reaction mechanisms and a kinetic model were proposed to quantitatively explain the dependence of F and HF number densities on power and pressure.

Here, studies are presented of CH_3F/CO_2 plasmas in the same ICP reactor used for the CH_3F/O_2 plasma. Absolute and relative species number densities and plasma beam-deposited film compositions and deposition rates were measured and compared to those obtained in CH_3F/O_2 plasmas.

II. EXPERIMENT

The compact ICP reactor used in the present work was described previously.^{8–10} Plasma was generated in a 16 cm long, 3.6 cm i.d. water-cooled alumina tube, surrounded by a three-turn coil made of 1/4 in. o.d. copper tubing that was also water-cooled. Gas was fed into the reactor at one end, while the other end was open to a 34 cm diameter spherical chamber that was pumped by a 300 l/s turbomolecular pump backed by a roughing pump. A trace rare gas (TRG) mixture containing 40% Ne, 20% Ar, 20% Kr, and 20% Xe was added to the feed gas for optical emission actinometry measurements. The total flow rate of $CH_3F + CO_2$ was 10 sccm, and the TRG flow rate was 0.3 sccm. The measured pressure upstream of the reactor was 10 mTorr. Since there was a

a)Electronic mail: vmdonnelly@uh.edu

b)Electronic mail: economou@uh.edu

pressure drop along the discharge tube, the average pressure in the reactor was about 8.5 mTorr.

The coil was driven by a radio frequency power supply at 13.56 MHz, through an impedance-matching network. Light emanating along the axis of the plasma was directed at one of three spectrometers (Ocean Optics model HR4000 with 1.7 Å resolution) covering the wavelength ranges of 200–427, 578–775, and 734–916 nm. Optical emission spectra were recorded after signals had reached steady-state levels.

Experiments were conducted as a function of the $CH_3F:CO_2$ feed gas flow ratio at a power of 300 W, and as a function of power (5–400 W) at a flow ratio of $CH_3F:CO_2 = 2:8$ sccm. At this flow ratio, the reactor walls were polymer-free.

III. RESULTS AND DISCUSSION

A. Optical emission spectral features

A typical emission spectrum is shown in Fig. 1. Emitting species included H (656.14 nm, E = 12.03 eV), F (685.60 nm, E = 14.5 eV), O (844.51 nm, E = 10.94 eV), C(247.7 nm, E = 7.65 eV), CO $(b^3 \Sigma^+ \rightarrow a^3 \Pi)$ (0,1) at 296.65 nm (E = 10.34 eV), $\text{CO}_2^+({}^2\Sigma_u^+ \rightarrow {}^2\Pi_g)$ at 289 nm ($E_{ip} + E = 13.77 + 4.27 \text{ eV}$), $\text{HF}^+(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi)$ at 390 nm $(E_{ip} + E = 16.04 + 3.14 \text{ eV}), CF(B^2 \Delta_r \rightarrow X^2 \Pi_r) \text{ at } 202.62 \text{ nm}$ $(E = 6.09 \text{ eV}), \text{ CH}(A^2 \Delta \rightarrow X^2 \Pi) (0,0) \text{ at } 431.25 \text{ nm} (E$ = 2.86 eV), and $OH(A^2\Sigma \rightarrow X^2\Pi)$ at 306.4 nm (*E* = 4.03 eV), where E_{ip} is the first ionization potential of CO₂ or HF, and E is the energy of the emitting species above its ground state. The CF peak at 202.62 nm is much weaker than other peaks, so it is not visible in Fig. 1. Relative and in several cases absolute number densities were obtained using the emission intensities from selected species, divided by the emission intensity from Ar at 750.39 nm (E = 13.48 eV) or Xe at 834.68 nm (E = 11.04 eV) to compensate for changes in the electron number density and energy distribution. Intensities of atomic and molecular



Fig. 1. Optical emission spectrum of a CH_3F/CO_2 inductively coupled plasma. Power = 300 W. Pressure = 10 mTorr. Flow rates (sccm) were $CH_3F:CO_2:TRG = 2:8:0.3$. TRG = trace rare gases (a mixture of 40%Ne, 20%Ar, 20%Kr, and 20%Xe).

J. Vac. Sci. Technol. A, Vol. 33, No. 2, Mar/Apr 2015

emissions were integrated over the respective bands (or for HF^+ over a single rotational line) and divided by accumulation times.

B. Power dependence

Emission intensities of Ar (750.39 nm) and Xe (834.68 nm), normalized to unity at 400 W, are plotted as a function of power in Fig. 2. The power dependences of Ar and Xe emissions are very similar to one another as found in previous work.⁹ A transition from a capacitively coupled mode to an inductively coupled mode (E-to-H transition) is evident near 40 W (see inset in Fig. 2). The Ar 750.39 nm line (Paschen 2p₁ level, E = 13.48 eV) is a good match for the energy of emitting levels of H, O, and F, and is free from electron impact out of the metastable state;¹¹ hence, this line was used for optical emission actinometry¹² to obtain number densities for these species as a function of power.

Absolute number density ratios n_H/n_{Ar} , n_O/n_{Ar} , and n_F/n_{Ar} , for H, O, and F, relative to Ar, were determined from actinometry and calibration procedures discussed previously.⁹ Values are presented in Fig. 3 as a function of power. Absolute number densities for Ar are also shown, assuming the same gas temperature as measured previously in CH₃F/O₂ plasmas.⁹ The measured emission intensities, I_X , from H, O, and F, integrated over the spectrometer broadened linewidth, were divided by the integrated intensity, I_A , of Ar 750.39 nm emission. Since the H/Ar, O/Ar, and F/Ar emission ratios were always taken from the same spectra (i.e., the same spectrometer), there was no need to divide by the accumulation time in this case. The H, O, or F number densities, n_X , are given by⁹



FIG. 2. Relative Ar 750.4 and Xe 834.7 nm emission intensities as a function of power. Pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂:TRG = 2:8:0.3. Measured Ar and Xe emission intensities were divided by 1517 and 3053, respectively, to normalize values to unity at the highest power. The inset shows the low power region and the break in the curves near 40 W, due to a transition from capacitive to inductive coupling. TRG = trace rare gases.



FIG. 3. (Color online) n_H/n_{Ar} , n_F/n_{Ar} , and n_O/n_{Ar} absolute number density ratios vs power. Pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂: TRG = 2:8:0.3. Absolute number densities for Ar are also shown, assuming the same gas temperature as measured previously in CH₃F/O₂ plasmas (Ref. 9). TRG = trace rare gases.

where n_A is the rare gas (i.e., Ar) number density, γ_X and γ_A are relative sensitivities of the spectrometer for the wavelengths at which X and A emit, and a_X is a proportionality constant, given in Table I, along with the corresponding references. The F 685.60 nm emission was chosen instead of the more commonly used 703.75 nm line because of spectral congestion in the 704 nm region, caused by emissions from CO at high CO₂ addition. To obtain a_X for the 685.60 nm line, spectra were recorded under conditions (100% CH₃F) that produced much less congestion around 704 nm, and the intensities of the 685.60 and 703.75 lines (I_{686} and I_{704}) were recorded. The ratio $I_{F,704}/I_{F,686}$ was found to be 0.586. The proportionality constant for the 685.60 nm line, was then calculated by $a_{F,686} = a_{F,704} (I_{F,704} / I_{F,686}) (\gamma_{686} / \gamma_{704})$, where the sensitivity ratio $\gamma_{686}/\gamma_{704} = 1.11$ was obtained from the calibration of the spectrometer with a standard tungsten filament lamp traceable to the National Institute of Standards. Therefore, $a_{F.686} = 1.85$.

Actinometry can provide estimates of relative and absolute number densities as plasma conditions vary, provided that the emission results primarily from electron impact excitation of the species of interest, and not from dissociative excitation of larger molecules.^{15,16} If the latter becomes dominant at low power, it will lead to an apparent number density that is independent of power. From Fig. 3, it appears that dissociative excitation is not becoming dominant at the lowest power at which intensities could be easily measured;

TABLE I. Actinometric parameters for different species.

Species (X)	$\lambda_{\rm X} ({\rm nm})$	$\alpha_{\rm x}$	$\gamma_{\rm Ar}/\gamma_X$	Reference
Н	656.14	1.6	0.51	13
0	844.51	0.62	2.5	14
F	703.75	2.84	0.61	9
F	685.60	1.85	0.54	9, this work
СО	296.65	3.28	_	9, 10, this work
CO ₂	289	1.9		This work

JVST A - Vacuum, Surfaces, and Films

hence, above 100 W, n_X/n_{Ar} measurements are a reliable measure of number densities.

Figure 4 presents absolute CO number densities, divided by Ar number densities. It should be noted that very little CO emission is produced by dissociative excitation of CO_2 , since the CO-to-Xe emission ratio extrapolates to zero at zero power. $n_{\rm CO}/n_{\rm Ar}$ values are given in Fig. 4, even though Xe emission was used to obtain the values. The reason is that Xe is pumped by the vacuum system at roughly half the rate as Ar under these transitional (but more Knudsen) flow conditions, while Ar is pumped at a similar rate to the average species in the plasma, including CO. The correction for the difference in effective pumping speed for CO relative to CO₂ was also carried out. The relative CO-to-Xe 834.7 nm (energy of the $2p_3$ excited state = 11.05 eV) emission ratios were converted into absolute number densities by making use of the "self-actinometry" calibration procedure that was carried out in a previous study.¹⁰ Briefly, small amounts of CO were added to the discharge and the resulting small increases in CO emission recorded. After verifying that little CO was dissociated in the plasma (because CO has a very large bond strength of 11.1 eV), and with small corrections for the slight perturbation of the plasma by trace CO addition, the increase in CO emission could be used to obtain the total amount of CO present.

Measurements of CO-to-Xe emission intensity ratios as a function of power were also made and these relative values were in good agreement with the change in CO number density with power, obtained by the self-actinometry method. This allows a calibration factor, $a_{\rm CO}$, to be obtained. (The spectrometer response factor $\gamma_{750}/\gamma_{297}$ was lumped into $a_{\rm CO}$, since the sensitivity of the ultraviolet spectrometer was not



FIG. 4. (Color online) $n_{\rm CO}/n_{\rm Ar}$, $n_{\rm CO_2}/n_{\rm Ar}$, and $n_{\rm CO}/n_{\rm Ar} + n_{\rm CO_2}/n_{\rm Ar}$ absolute number density ratios vs power. Pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂:TRG = 2:8:0.3. Absolute number densities for Ar are given in Fig. 3, assuming the same gas temperature as measured previously in CH₃F/O₂ plasmas (Ref. 9). In the sum of $n_{\rm CO}/n_{\rm Ar} + n_{\rm CO_2}/n_{\rm Ar}$, the CO number densities were corrected for the pumping speed difference relative to CO₂. TRG = trace rare gases. For CO, error bars represent the combined uncertainty from the actinometry method (±20%) and the ±15% scatter of the data used to obtain the calibration factor for converting emission ratios to CO-to-Ar number density ratios. The error bars for CO₂ are mainly due to the ±10% scatter in the data below 40 W that are used to calibrate the measurement.

determined; hence, the proportionality constant is only valid for the spectrometers used in these experiments.) In the previous study, the CO-to-Xe number density ratio at 300 W was found to be 40.3 at a Xe-to-total feed gas ratio of 0.00513, corresponding to a CO number density of 2.9×10^{13} cm⁻³ at a measured gas temperature of 640 K.^{9,10} Under the present conditions, the integrated CO-to-Xe band intensity ratio, corrected for accumulation time differences and uncorrected for spectrometer response differences at the two wavelengths, was 12.3. Hence, $a_{\rm CO} = 40.3/12.3 = 3.28$ (Table I). $n_{\rm CO}/n_{\rm Xe}$ rises sharply with power between 20 and 70 W, as the plasma transitions from E to H mode, and then increases much more slowly between 100 and 400 W, where little CO dissociation occurs. The error bars for CO in Fig. 4 represent an approximate $\pm 20\%$ uncertainty in the relative CO number density obtained by the actinometry method, combined with a $\pm 15\%$ scatter in the data that were used in previous and current work to obtain the calibration factor to convert relative emission ratios to absolute CO-to-Ar number density ratios.¹⁰

Measurements of CO_2^+ -to-Ar emission ratios are also presented in Fig. 4. These data are presented as CO_2 -to-Ar number density ratios in Fig. 4 because it is believed that CO_2^+ emission intensity is proportional to CO_2 number density, as discussed next. In the dim mode (E mode) below 40 W, we expect little dissociation of CO_2 with such a low electron density. Here, the emission ratio is independent of power, suggesting that CO_2^+ emission is a result of a single excitation step:

$$CO_2 + e^- \to CO_2^{+*} + 2e^-,$$
 (2)

$$\operatorname{CO}_2^{+*} \to \operatorname{CO}_2^+ + \mathrm{h}\nu. \tag{3}$$

If the two-step excitation process

$$\mathrm{CO}_2 + \mathrm{e}^- \to \mathrm{CO}_2^+ + 2\mathrm{e}^- \tag{4}$$

$$CO_2^+ + e^- \to CO_2^{+*} + 2e^-$$
 (5)

were important, then the CO₂⁺-to-Ar emission ratio should increase linearly with increasing power in the low power region (<40 W), since CO₂⁺ emission would scale with the square of electron density (n_e^2) , while Ar emission is linear with n_e . In the high density mode (H mode) of operation above 50 W, the emission ratio decreases roughly twofold between 50 and 100W and drops by almost half again between 100 and 200 W, due to electron impact dissociation of CO2. If the two-step excitation process were suddenly much more important than the single step process in the high density mode (H mode), we would expect the emission ratio between 50 and 200 W to lie between a fourfold increase if no CO₂ dissociates, to being nearly independent of power if CO_2 were being dissociated much faster than it reformed by recombination. Between 200 and 400 W, the emission ratio drops by a factor of \sim 1.4. It is not clear whether the two step excitation process or reformation of CO₂ by recombination of O and CO is becoming more significant at the highest powers investigated.

If we assume that the single step excitation process dominates at all powers, then we can use the extrapolation to zero power to calibrate the emission ratio in the limit of no dissociation of CO₂, where n_{CO_2}/n_{Ar} is equal to the input feed gas ratio of 133 (indicated by the arrow in Fig. 4). This then allows n_{CO_2}/n_{Ar} to be determined at all powers. The error bars represent predominantly the ±10% scatter in the data below 40 W, which are used to calibrate the measurements at all powers. n_{CO_2}/n_{Ar} falls to 22.2 at 400 W, meaning that the CO₂ feed gas is 83.3% dissociated. If the two-step excitation plays any role, then the degree of dissociation would be even higher in the 300–400 W region.

The sum of $n_{\rm CO}/n_{\rm Xe}$ and $n_{\rm CO_2}/n_{\rm Ar}$ is also plotted in Fig. 4. Since we expect little dissociation of CO in the discharge, this sum should be constant as a function of power, or even increase somewhat with power, due to reactions of O with C-containing species formed by dissociation of CH₃F. Instead, the sum decreases by ~20% between 30 and 400 W. Given the uncertainty in the actinometry method and calibration constants, the overall consistency is reasonable.

For the lower energy emitting species CH, CF, OH, and C, the Xe 834.7 nm line was used to produce the emission ratios contained in Fig. 5. For HF⁺, it was assumed that emission results from a single electron impact reaction, requiring a minimum of 19.18 eV, and so Ar 750.39 nm emission was used as the actinometer gas. HF⁺/Ar emission ratios in Fig. 5 are expected to be roughly proportional to relative HF number density, since there are no larger molecules that would likely produce HF⁺ emission. CH, CF, and C emission ratios are qualitative indicators of changes in relative number densities of these species, but could also contain contributions from larger molecules that contain these species, such as CHF. Emissions from CH does not arise from dissociative excitation of CH₃F, however, since emission ratios increase steeply with power, from near-zero extrapolated to zero power. Emission from OH is likely produced by electron impact on OH, with perhaps a dominant component



FIG. 5. (Color online) Normalized intensity ratios of CH/Xe, CF/Xe, HF^+/Ar , OH/Xe, and C/Xe emission vs power. Pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂:TRG = 2:8:0.3. The emission ratios were normalized by dividing measured intensities (divided by their respective accumulation times) by 4.2, 0.20, 0.072, 11.2, and 5.1 for CH/Xe, CF/Xe, HF^+/Ar , OH/Xe, and C/Xe, respectively, before plotting. TRG = trace rare gases.

J. Vac. Sci. Technol. A, Vol. 33, No. 2, Mar/Apr 2015

from dissociative excitation of $H_2O.^9$ CF and HF^+ emissions could not be measured below 150 and 90 W, respectively, due to weak intensities in this low power region. CH, CF, OH, and HF^+ in CH₃F/CO₂ plasmas show the same power dependence as was found for CH₃F/O₂ plasmas for the same power range.⁹

CH/Xe and OH/Xe behave similarly, rising first steeply with power, and then increasing much slower. The power dependence of C/Xe (nearly linear) is very different from that of CH/Xe or CF/Xe. This suggests that most C emission is produced by electron impact excitation of C (which forms when CH and CF begin to dissociate at the higher powers), and not by dissociative excitation of CH and CF.

C. Gas composition dependence and comparisons of CH_3F/O_2 and CH_3F/CO_2 plasmas

Using the calibration values in Table I, emission intensity ratios as a function of CO₂ feed gas percentage were converted into the absolute number density ratios n_H/n_{Ar} , $n_O/n_{\rm Ar}$, and $n_F/n_{\rm Ar}$ presented in Fig. 6. Number densities follow the expected dilution trends as a function of added CO₂ until reaching 75% CO₂, whereupon n_F/n_{Ar} , n_H/n_{Ar} , and $n_O/n_{\rm Ar}$ increase sharply by factors of 3.3, 1.6, and 3.4, respectively, before peaking. n_F/n_{Ar} and n_H/n_{Ar} resume a linear decrease with increasing CO₂. Interestingly, the O number density is 30% lower in a pure CO₂ plasma than it is in a 4% CH₃F/96% CO₂ plasma. A similar effect was observed when small amounts of CF_4 were added to an O_2 plasma.^{17,18} The sharp increase in F and O number density observed above 75% CO2 addition is similar to that found previously in CH₃F/O₂ plasmas and ascribed to a transition from polymer-covered to polymer-free walls above a specific O₂ feed gas percentage ($48\% O_2$).

Comparisons between key species in CH_3F/O_2 and CH_3F/CO_2 plasmas as a function of added O_2 or CO_2 are summarized in Figs. 7–9. To improve the precision of the comparisons, measurements in CH_3F/O_2 plasmas, reported previously,⁸ were repeated within about one month after the



FIG. 6. (Color online) n_F/n_{Ar} , n_H/n_{Ar} , and n_O/n_{Ar} absolute number density ratios as a function of %CO₂ addition. Pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂:TRG = 2:8:0.3. Power = 300 W. TRG = trace rare gases.



FIG. 7. (Color online) Normalized number density ratios for $n_{H/}n_{Ar}$, n_{F}/n_{Ar} , and n_{O}/n_{Ar} , and normalized intensity ratios for HF⁺/Ar, as a function of CO₂ or O₂ addition with a constant total flow rate of 10.3 sccm, including 0.3 sccm TRG, at a pressure of 10 mTorr, and a power of 300 W. TRG = trace rare gases.

CH₃F/CO₂ measurements, with the same reactor configuration. In addition, because of variations in placement of the three spectrometers that were frequently exchanged, and drift in the small flow rate of the rare gases (0.3 sccm), species-to-rare gas (Ar or Xe) emission ratios were normalized in one of several ways. For F, H, HF⁺, CH, CF, and C, intensity measurements were normalized to those carried out in CH₃F plasmas, shortly before or after operating CH₃F/O₂ or CH₃F/CO₂ plasmas. For CO, CO₂, and OH, measurements were normalized to the nearby HF⁺ emission in CH₃F plasmas. For example, if the HF^+ emission in the pure CH_3F plasma spectrum recorded in the set of measurements with added CO₂ were twice that of the pure CH₃F plasma in the set of measurements with added O₂, then all CO, CO₂, and OH intensities in the CO_2 addition experiment were multiplied by 0.5. For O, intensities were normalized to the second order CH and H_{γ} emissions in pure CH₃F plasmas that were observed nearby at 862.6 and 868.1 nm, respectively.



FIG. 8. (Color online) Normalized intensity ratios of CH/Xe, CF/Xe, C/Xe, and OH/Xe emission as a function of CO_2 or O_2 addition with a constant total flow rate of 10.3 sccm, including 0.3 sccm TRG, at a pressure of 10 mTorr, and a power of 300 W. TRG = trace rare gases.

JVST A - Vacuum, Surfaces, and Films



FIG. 9. (Color online) $n_{\rm CO}/n_{\rm Ar}$ and $n_{\rm CO_2}/n_{\rm Ar}$ absolute number density ratios as a function of CO₂ or O₂ addition with a constant total flow rate of 10.3 sccm, including 0.3 sccm TRG, at a pressure of 10 mTorr, and a power of 300 W. TRG = trace rare gases.

These intensities were then divided by Ar (for H, F, O, HF⁺ and CO₂⁺) or Xe (for CO, CH, CF, C, and OH) emission as a function of added CO₂ and O₂. Finally, for H, F, O, CO, and CO_2 , the species-to-rare gas emission ratios were obtained at 300 W for 50%CH₃F/50%O₂ plasmas and 20%CH₃F/80%CO₂ plasmas. These emission ratios were then multiplied by the appropriate actinometry constants in Table I to obtain absolute number densities for these two conditions, which in turn were used to calibrate all other values for H, F, O, CO, and CO₂ in Figs. 7 and 9. The remaining emission ratios (Fig. 8) were left as normalized values; however, a comparison between CO₂ and O₂-containing plasmas is still valid. As was done in the power dependence measurements in Fig. 4, $n_{\rm CO}/n_{\rm Ar}$ values are given in Fig. 9, instead of $n_{\rm CO}/n_{\rm Xe}$ for reasons given above, and corrections were made for the difference in effective pumping speed for CO relative to CO₂. The error bars in Fig. 9 at 20%CH₃F/80%O₂ or CO₂ present the standard error in the average of several experiments.

At any given addition of $\leq 40\%$ O₂ or CO₂, O/Ar, F/Ar, H/Ar, C/Xe, CH/Xe, CF/Xe, HF⁺/Ar, and CO/Ar number densities or emission ratios are nearly identical, indicating (for F, O, H, CO, and HF) or suggesting (for CF, CH, and possibly C) that number densities for these species behave in a similar manner in CH₃F/CO₂ and CH₃F/O₂ plasmas. At $\geq 80\%$ addition, F and H number densities are also independent of whether the additive is O₂ or CO₂, while O number densities in CH₃F/O₂ plasmas are about twice those in CH₃F/CO₂ plasmas. CO and CO₂ are all larger in CH₃F/CO₂ plasmas for $\geq 80\%$ CO₂, as expected.

Between the transitions from net film deposition to no deposition (48% for O_2 to ~75% for CO_2), O, F, and H number densities in CH₃F/O₂ plasmas increase sharply to exceed

those in CH₃F/CO₂ plasmas (Fig. 7), because they are no longer consumed by etching a film in O₂-containing plasmas. CF/Xe, and to a small extent CH/Xe, behave similarly; presumably, they are no longer lost growing a film in CH₃F/O₂ plasmas. The most substantial differences between CH₃F/O₂ and CH₃F/CO₂ plasmas are the much lower OH/Xe emission ratios and much higher CO₂/Ar number density ratios in CH₃F/CO₂ plasmas, throughout the range of gas addition.

C/Xe emission ratios in the two plasmas are similar up to 60% addition, whereupon those in O2-containing plasmas drop rapidly, while the emission ratios in CO₂-containing plasmas do not change much up to the limit of pure CO₂ (Fig. 8). Since C/Xe emission ratios exhibit the opposite behavior as CH/Xe and CF/Xe emission ratios-increasing with increasing% CO₂ in the feed gas—it appears that C emission is not predominantly as a result of dissociative excitation of any CH_xF_y species. C/Xe emission ratios behave in a similar manner to CO/Xe number density ratios as a function of added CO₂, suggesting that dissociative excitation of CO, as well as emission from electron impact on C produced from dissociation of CO, is the major sources of this emission in CO₂-rich plasmas. Conversely, in pure CH₃F plasmas, large C/Xe emission ratios were recorded, indicating that under CH₃F-rich conditions, the predominant source of C emission is likely to be electron impact excitation of C.

D. Mechanisms

Previously it was shown that under conditions that do not deposit a hydrocarbon film on the reactor walls (i.e., $O_2 \ge 48\%$), the fluorine atom number density in high density CH_3F/O_2 ICPs is approximately given by the expression

$$n_F \approx \frac{2n_{\mathrm{CH}_3\mathrm{F}}^0 k_d n_e}{k_a \left[3n_{\mathrm{CH}_3\mathrm{F}}^0 \left(\frac{T^0}{\bar{T}_g} \right) - S_H n_H \right] + k_{a,w} + k_{\mathrm{pump}}} \left(\frac{T^0}{\bar{T}_g} \right), \tag{6}$$

where n_e is the electron number density, $n_{CH_3F}^0$ is the CH₃F feed gas number density with the plasma off, and T_g represents the mean gas temperature in the discharge tube, taken as the average of T_g (the measured temperature at the center of the tube) and the wall temperature of $T^0 = 300 \text{ K}$ (ignoring a small thermal slip). S_H (=3.6) is the computed conductance of H divided by the average conductance of the gases. It was assumed that the electron impact rate coefficients, k_d $(=1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1})$, for destruction of HF and CH_xF were similar for all values of x, and that gaseous abstraction reactions of H by F proceed with the same rate coefficient $(k_a = 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})$ for all H-containing molecular species, taken as the average of the known abstraction rate coefficients for H₂, H₂O, and CH₃F. Rate coefficient, k_{pump}, accounts for loss of F through pumping at the reactor exit, and $k_{a,w}$ is a first-order rate for abstraction by F of H on the wall. With these added terms, the above expression is valid as the % CH₃F in the feed gas goes to zero, and/or as power goes to infinity. With trace added Ar, the F-to-Ar number density ratio is

where n_{Ar}^{0} is the Ar number density in the feed gas with the power off. (Note: In a previous publication,⁹ the term $S_H n_H$ was erroneously given as $S_H n_H / n_{Ar}$. The implications of this error on model predictions reported in that publication are discussed below.)

Under the experimental conditions, diffusion is facile and the F-atom loss at the walls is limited by the surface reaction.¹⁰ Thus, $k_{a,w}$ can be expressed as

$$k_{a,w} = \frac{\gamma}{2(2-\gamma)} \frac{\bar{\nu}_F A}{V},\tag{8}$$

where \bar{v}_F is a mean thermal velocity for F, and A and V are the chamber surface area and volume. For length L = 16 cmand radius R = 1.8 cm, A = 181 cm², and V = 163 cm³. Here, γ is the probability for abstraction by an impinging F atom of an H atom from the hydrocarbon film on the reactor wall under CH₃F-rich conditions, or from a "clean" wall under CH₃F-lean conditions. Given the large cross sections for Habstraction by collisions of F with hydrocarbon molecules in the gas phase, we would expect a large value ($\gamma \sim 0.5$) for F abstraction of H from a hydrocarbon film. Since F rises about threefold in going from hydrocarbon film-covered to filmfree conditions in both CH₃F/CO₂ and CH₃F/O₂ plasmas (Fig. 3), then we expect $\gamma < 0.1-0.2$ for clean walls. (It could be much less than 1/3 of 0.5, since gas phase H-abstraction reactions may be faster than the heterogeneous reaction under clean wall conditions.)

Fluorine-to-Ar number density ratios as a function of power were computed from Eq. (7) for 20% CH₃F/80% CO₂ plasmas, using n_e and T_g measured in 50% CH₃F/50% O₂ plasmas (n_e and T_g were not measured in 20% CH₃F/80% CO_2 plasmas). n_F/n_{Ar} values were also computed as a function of power in 50% CH₃F/50% O₂ plasmas to compare with previous measurements.⁹ γ was treated as the only adjustable parameter. The predicted n_F/n_{Ar} values represented by the thick red and blue lines in Fig. 10 are in good agreement with the measurements with $\gamma = 0.23$ for CO₂ and 0.17 for O_2 -containing plasmas. Within the uncertainties of the experiment, there is no significance difference in these γ values for the two plasmas. Between 300 and 400 W, the predicted n_F/n_{Ar} values in CH₃F/CO₂ plasmas continue to increase with power, while the measurements appear to be reaching a plateau at the highest powers. In the previous model predictions for CH₃F/O₂ plasmas, use of the incorrect term $S_H n_H / n_{\rm Ar}$, discussed above, caused the model to erroneously predict $\gamma = 0$ for clean walls.

Equation (7) was also used to predict n_F/n_{Ar} as a function of gas composition for the CH₃F/CO₂ plasmas in the present study and for the CH₃F/O₂ plasmas reported previously.⁹ It should be noted that n_F/n_{Ar} measurements reported previously for CH₃F/O₂ plasmas are roughly twice those found in

1.5 Ar 10 8 $n_{\chi}^{/}n_{A_{\Gamma}}$ 6 F/Ar (C 0.5 2 0 0.0 200 250 50 100 150 300 350 400 0 Power (W)

FIG. 10. (Color online) n_F/n_{Ar} vs power. Total pressure = 10 mTorr. Flow rates (sccm) were CH₃F:CO₂:TRG = 2:8:0.3 or CH₃F:O₂:TRG = 4.75:4.75: 0.25 from a previous study (Ref. 9). Absolute number densities for Ar are also shown, assuming the same gas temperature as measured previously in CH₃F/O₂ plasmas (Ref. 8). The solid lines are model predictions from Eq. (7), with γ = 0.23 for CO₂ and 0.17 for O₂. TRG = trace rare gases.

the present study for CH_3F/O_2 plasmas (compare Fig. 7 with Fig. 11). Changing wall conditions, drift in mass flow controllers (especially for the very low TRG flow) and repeatability in the placement of the spectrometers could all contribute to this discrepancy.

Model predictions are represented by the thick red and blue solid lines in Fig. 11. The values for γ needed to reproduce the $n_F/n_{\rm Ar}$ measurements are given in Fig. 12. For CH₃F-rich plasmas γ is very large (0.5–0.9). For both plasmas, there appears to be a small increase in γ between pure CH₃F and roughly 30% CO₂ or O₂ addition. The drop in γ in CH₃F/O₂ plasmas at 48%–49% O₂ is very abrupt to a value of 0.23. Beyond this point, γ continues to decrease linearly with further O₂ addition, reaching a very low value of <0.02 at 85% O₂. For CH₃F/CO₂ plasmas, a similar drop in γ is



FIG. 11. (Color online) n_F/n_{Ar} as a function of CO₂ or O₂ addition with a constant total flow rate of 10.3 sccm, including 0.3 sccm TRG, at a pressure of 10 mTorr, and a power of 300 W. The solid lines are model predictions from Eq. (7). See text for details. The values for the adjustable parameter, γ , required to match the model predictions to the observed n_F/n_{Ar} values, are given in Fig. 12. TRG = trace rare gases.



FIG. 12. (Color online) Reaction probabilities, γ , the only adjustable parameter in the model, for abstraction of H from the reactor walls by impinging F in CH₃F/CO₂ and CH₃F/O₂ plasmas, using the data in Fig. 11.

found near 75% CO_2 , but the transition to a lower value is more gradual.

E. Film growth

The abrupt change in species concentrations observed previously in CH₃F/O₂ plasmas near 48% added O₂ was attributed to a transition from hydrocarbon-covered reactor walls below 48% O_2 to film-free walls above 48% O_2 .⁸ This was based on indirect evidence. Here, the abrupt change in species concentrations observed near 75% CO₂ addition was attributed to the same effect. This has also been observed with x-ray photoelectron spectroscopy (XPS) measurements, as reported in another study.¹⁹ In that investigation, the substrate was placed in an evacuated chamber 10 cm from the open, downstream end of the plasma tube. Film compositions as well as deposition rates were determined; the latter are summarized in Fig. 13. Deposition rates decrease with increasing O₂ or CO₂ addition, reaching zero near 40% O₂ and 70% CO₂, supporting the explanation for the abrupt increase in F and O number density observed here and



Fig. 13. Deposition rates on p-Si substrates placed 10 cm from the open, downstream end of the plasma tube, in CH_3F/O_2 and CH_3F/CO_2 plasmas at 300 W and 10 mTorr.

J. Vac. Sci. Technol. A, Vol. 33, No. 2, Mar/Apr 2015

previously.⁸ Films deposited on p-Si in CH₃F-containing plasmas with 10% O₂ or CO₂ contained F:O:C in a ~2:1:7 ratio. The C(1 s) spectra contained a strong peak near 284.3 eV, attributed to CH, CH₂ and/or graphitic carbon, and weaker features at 286.4 eV (CO) and 288.8 eV (CF). As the O₂ or CO₂ content in the plasma increased, the contributions of the 286.4 and 288.8 eV features increased relative to the 284.3 eV main peak. For similar deposition rates, there were no substantial differences between films deposited in CH₃F/O₂ vs CH₃F/CO₂ plasmas.

Deposition rates for films deposited downstream of the plasma are much slower than for the film deposited on the walls of the discharge tube. The maximum possible deposition rate (in Å/min) for the wall deposits can be obtained from carbon mass balance in the plasma, assuming that CO and CO₂ are the dominant nondepositing forms of carbon in the discharge:

$$R_{\rm dep}^{\rm max} = \frac{2.6 \times 10^{27} M_{\rm film}}{A N_A \rho_{\rm film}} \left(f_{\rm CH_3F}^{\rm in} + f_{\rm CO_2}^{\rm in} - f_{\rm CO_2}^{\rm out} - f_{\rm CO}^{\rm out} \right),$$
(9)

where f^{in} and f^{out} are the input and output flow rates for the subscripted species, M_{film} and ρ_{film} are the molecular mass and density of the deposited film, respectively, $A \ (=181 \text{ cm}^2)$ is the reactor surface area, and N_A is Avogadro's number. The film was assumed to have a stoichiometry of $\text{CH}_2\text{O}_{1/7}\text{F}_{2/7}$ (C, O, and F from XPS) and a density of about that of polyethylene, thus $M_{\text{film}} = 21.7 \text{ g/mol}$ and $\rho_{\text{film}} = 1 \text{ g/cm}^3$. The output flow rates were $f_{\text{CO}}^{\text{out}} = f_{\text{Ar}}^{\text{in}} n_{\text{CO}_2} / n_{\text{Ar}}$ and $f_{\text{CO}}^{\text{out}} = f_{\text{Xe}}^{\text{in}} n_{\text{CO}} / n_{\text{Xe}}$, where the Ar and Xe input flow rates were $f_{\text{Xe}}^{\text{in}} = 0.06$ sccm.

Maximum deposition rates computed from Eq. (9) as a function of CO₂ or O₂ addition are plotted in Fig. 14. The trends qualitatively match the observations in that deposition rates are faster with CO₂ addition, and drop to a low rate at about 50% O₂, or 70% CO₂. Predicted deposition rates on the discharge walls are much larger (\sim 20 to 100 times) than the observed rates for the expanded plasma beam (Fig. 13), as expected.



FIG. 14. (Color online) Maximum deposition rate as a function of CO_2 or O_2 addition, computed from Eq. (9) and using the data in Fig. 9, corresponding to a pressure of 10 mTorr and a power of 300 W.

F. Thermodynamic equilibrium

Thermodynamic equilibrium calculations were performed to determine the most prominent species in CH₃F/CO₂ and CH₃F/O₂ gas mixtures at 10 mTorr and a temperature of 373 K. While the plasma is far from thermodynamic equilibrium, such calculations provide insights into what species can be expected to form or not form when the feed gases are largely dissociated into atoms and diatomic molecules. Relative abundances of species are plotted as a function of CO₂ or O₂ addition in Fig. 15. The major gaseous components HF, H₂O, CH₄, and H₂ are nearly identical in CH₃F/CO₂ and CH₃F/O₂ plasmas at all gas additions. Below 60%, CO₂ concentrations are also equivalent. Above 60%, CO₂ rises linearly, with further CO₂ addition [Fig. 15(a)], and O₂ rises from near zero, with further O₂ addition [Fig. 15(b)]. The rise in O₂ above 60% added O₂ corresponds to the overall reaction

$$CH_3F + \frac{3}{2}O_2 \rightarrow CO_2 + HF + H_2O$$
(10)

reaching the stoichiometric mixture. Above 60% O₂, the excess O₂ builds up.

The most significant difference between CH_3F/CO_2 and CH_3F/O_2 plasmas is the much larger amount of solid carbon at thermodynamic equilibrium at all percentages of CO_2 addition compared to O_2 addition.

G. Possible deposition precursors

Film deposition rates for CH_3F/CO_2 plasmas are faster than those for CH_3F/O_2 plasmas between 10% and 40% CO_2



Fig. 15. (Color online) Relative abundance of the most prominent species at thermodynamic equilibrium as a function of CO_2 or O_2 addition to CH_3F at 10 mTorr and a temperature of 373 K.

or O_2 (Fig. 13). The observed deposition rate is a net rate of deposition minus etching. Deposition precursors CH and C appear to be present at similar levels in these plasmas. Other possible precursors include CH₃, CH₂F, CH₂, and CHF. While it is possible that the number density of one or more of these species is higher in CO₂-containing plasmas, it is not clear how this could be the case. These species are both generated by electron impact on CH₃F, and for CH₂ and CHF, by additional electron impact on CH₃ and CH₂F. The only fast gas phase reactions that destroy or form these species are with O, H, and F, occurring at 10%-100% of gas kinetic rates. But the number densities of O, H, and F are nearly the same for O2 and CO2 additions between 10% and 40%. Any reactions of CH_x and CH_xF species with CO, CO₂, HF, and H₂O are slow or do not occur at 300-500 K. Apparently, C₂-containing and higher hydrocarbons are not formed, since C₂ and C₃ emissions, sensitive indicators of the presence of these species were not observed.⁹ CO_2 is not a deposition precursor. Hence, it seems likely that the fluxes of all deposition precursors are similar in CH₃F/CO₂ and CH₃F/O₂ plasmas between 10% and 40% gas addition.

The films are etched by O atoms, and could also be etched by F and H atoms. Again, these atomic species are similar in the two plasmas below 40% addition of CO_2 or O_2 ; hence, the film etching rates by the sum of these species should be similar. Perhaps OH could also etch the film. The most significant difference at $\leq 40\%$ CO₂ and O₂ addition is the $\sim 2 \times$ larger OH/Xe emission ratios in CH₃F/O₂ plasmas, consistent with its slower film deposition rates if OH were to etch the film. OH and H₂O would also be expected to adsorb and have long residence times on the surface, possibly blocking adsorption by deposition precursors preferentially in CH₃F/O₂ plasmas and thereby slowing film deposition rates. While the detailed kinetics and mechanisms by which faster deposition rates occur in CH₃F/CO₂ plasmas remains unknown, thermodynamic equilibrium will tend to drive enhanced deposition of solid carbon in CH₃F/CO₂ relative to CH_3F/O_2 gas mixtures (Fig. 15).

No published studies, other than those of this laboratory, could be found for plasma decomposition of CH_3F with added O_2 or CO_2 . The homogeneous and heterogeneous chemistry of CHF_3 -containing plasmas has been widely reported, but is very different because the complete conversion of the feed gas to HF leaves fluorocarbon and not hydrocarbon precursors for deposition and etching. Our results can be compared with studies by Teii *et al.*²⁰ for 80 mTorr CH_4 ICPs with added O_2 or CO. They found that deposition of diamond and nondiamond forms of carbon was enhanced with CO addition and that diamond deposition was suppressed with O_2 addition. These trends are similar to those found in the present study for CO_2 vs O_2 addition. Other trends that were found in that study, such as formation of C_2 were not found in the present study.

IV. CONCLUSIONS

A CH_3F/CO_2 inductively coupled plasma was investigated as a function of power (5–400 W) and feed gas

JVST A - Vacuum, Surfaces, and Films

composition, at a pressure of 10 mTorr, using optical emission spectroscopy and rare gas actinometry. Absolute H, F, and O number densities increased with power in CH₃F/CO₂ (20%/80%) plasmas, reaching 4.0, 0.34, and 1.6×10^{13} /cm³, respectively, at 300 W. Under these conditions, the reactor wall was polymer-free. A calibration factor $a_{\rm CO}$ was obtained from previous self-actinometry experiments in CH₃F/O₂ plasmas, allowing the estimated CO number density of 8.8×10^{13} /cm³ in a 300 W CH₃F/CO₂ plasmas to be obtained from the CO/Xe emission intensity ratio. As power increased above 40 W, CO₂ was increasingly dissociated reaching a degree of dissociation of at least 83% at 400 W.

The number densities of H, F, and O were observed to increase abruptly between 74% and 80% CO₂ by 1.6, 3.3, and 3.4, respectively, ascribed to the transition from polymer-covered to polymer-free reactor walls as increasing CO₂ additions caused the wall polymer etching rate to exceed the deposition rate, similar to that at 48% O₂ in CH₃F/O₂ plasmas. Number densities (F/Ar, H/Ar, O/Ar, and CO/Xe) or emission intensity ratios (C/Xe, CH/Xe, CF/Xe and HF^+/Ar) were nearly equal in CH_3F/CO_2 and CH_3F/O_2 plasmas. The most substantial differences were the lower OH/Xe emission ratios and higher CO₂/Ar number density ratios with CH₃F/CO₂ feed gas. A model from previous work was used to predict F/Ar number density ratios as a function of power and feed gas composition. The model was used to estimate the probability (γ) of hydrogen abstraction from the wall by F atoms as a function of O₂ or CO₂ addition. The value of γ (the only adjustable parameter in the model) was higher in CH₃F/CO₂ plasmas and dropped abruptly when the wall transitioned from polymer-coated to polymer-free.

Films deposited on p-Si substrates placed 10 cm from the open, downstream end of the plasma tube, in both CH₃F/O₂ and CH₃F/CO₂ plasmas, were studied by XPS. Deposition rates were faster in CH₃F/CO₂ plasmas at the same O₂ or CO2 addition. For similar deposition rates, no substantial differences were observed in C(1s) spectra. Deposition ceased above percentages of CO_2 (75%) and O_2 (48%) at which the abrupt increases in F, H, and O emissions were found. Maximum possible deposition rates on reactor walls as a function of gas addition, obtained from carbon mass balance by assuming that CO and CO₂ are the dominating and nondepositing forms of carbon, qualitatively matched the observed relative deposition rates. Thermodynamic equilibrium calculations were performed for the feed gas composition of both plasmas. Much more solid carbon would form in all percentages of the CH_3F/CO_2 gas mixture at equilibrium for a pressure of 10 mTorr and temperature of 373 K. This could explain higher deposition rates in $CH_3F/$ CO_2 plasmas. The higher OH and/or H_2O found in CH_3F/O_2 plasmas could also slow deposition relative to CH_3F/CO_2 plasmas by blocking the adsorption of deposition precursors on the surface, or etching by OH.

ACKNOWLEDGMENTS

The authors are grateful to Lam Research and the Department of Energy, Office of Fusion Energy Science, contract DE-SC0001939, for financial support of this work.

- ¹V. Jovanovic, T. Suligoj, M. Poljak, Y. Civale, and L. K. Nanver, Solid-State Electron. **54**, 870 (2010).
- ²O. Joubert *et al.*, **Proc. SPIE 8328**, 83280D (2012).
- ³K. J. Kanarik, G. Kamarthy, and R. A. Gottscho, Solid State Technol. **55**, 15 (2012).
- ⁴Y. Wang and L. Luo, J. Vac. Sci. Technol., A 16, 1582 (1998).
- ⁵L. L. Chen, L. D. Xu, D. X. Li, and B. Lin, Microelectron. Eng. **86**, 2354 (2009).
- ⁶R. Blanc, O. Joubert, T. David, F. Leverd, and C. Verove, in *Meeting Abstracts* (The Electrochemical Society Honolulu PRiME, 2012), Vol. 39, p. 2926.
- ⁷Y. Iijima, Y. Ishikawa, C. Yang, M. Chang, and H. Okano, Jpn. J. Appl. Phys., Part 1 36, 5498 (1997).
- ⁸E. Karakas, V. M. Donnelly, and D. J. Economou, Appl. Phys. Lett. **102**, 034107 (2013).
- ⁹E. Karakas, V. M. Donnelly, and D. J. Economou, J. Appl. Phys. **113**, 213301 (2013).
- ¹⁰E. Karakas, S. Kaler, Q. Lou, V. M. Donnelly, and D. J. Economou, J. Phys. D: Appl. Phys. 47, 085203 (2014).
- ¹¹J. B. Boffard, G. A. Piech, M. F. Gehrke, L. W. Anderson, and C. C. Lin, Phys. Rev. A **59**, 2749 (1999).
- ¹²J. W. Coburn and M. Chen, J. Appl. Phys. **51**, 3134 (1980).
- ¹³S. J. Kang and V. M. Donnelly, Plasma Sources Sci. Technol. 16, 265 (2007).
- ¹⁴N. C. M. Fuller, M. V. Malyshev, V. M. Donnelly, and I. P. Herman, Plasma Sources Sci. Technol. 9, 116 (2000).
- ¹⁵R. A. Gottscho and V. M. Donnelly, J. Appl. Phys. 56, 245 (1984).
- ¹⁶M. V. Malyshev and V. M. Donnelly, J. Appl. Phys. 88, 6207 (2000).
- ¹⁷M. A. Hartney, D. W. Hess, and D. S. Soane, J. Vac. Sci. Technol., B 7, 1 (1989).
- ¹⁸F. D. Egitto, F. Emmi, R. S. Horwath, and V. Vukanovic, J. Vac. Sci. Technol., B **3**, 893 (1985).
- ¹⁹S. Kaler, Q. Lou, D. J. Economou, and V. M. Donnelly, "X-ray photoelectron spectroscopy studies of silicon nitride and silicon etching in CH₃F/O₂ and CH₃F/CO₂ plasma beams," (unpublished).
- ²⁰K. Teii, H. Ito, M. Hori, T. Takeo, and T. Goto, J. Appl. Phys. **87**, 4572 (2000).