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Absolute fluorine atom concentrations in fluorocarbon plasmas determined from CF₂ loss kinetics

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We present a simple technique for determining the absolute fluorine atom concentration in pure CF₄ capacitively coupled radio-frequency discharges. It is based on the measurement, by laser-induced fluorescence, of the loss rate k_{loss} of the CF₂ radical in the afterglow of a pulsed plasma. We first demonstrate that in our conditions, CF₂ is lost only by gas phase recombination with F atoms (with a known rate constant k_{rec}) and by recombination at the reactor walls at a rate k_{wall} , independent of the rf power injected. Hence, the total CF₂ loss rate, $k_{\text{loss}} = k_{\text{wall}} + k_{\text{rec}}[F]$, varies linearly with $[F]$ when the rf power is increased. By recording k_{loss} and the relative variation of the F atom concentration (by optical emission actinometry) as a function of rf power, k_{wall} and $[F]$ can be determined. These measurements of $[F]$ complement previous quantitative measurements of CF and CF₂ radicals [Booth *et al.*, *J. Appl. Phys.* **85**, 3097 (1999); and Cunge and Booth, *J. Appl. Phys.* **85**, 3952 (1999)] made in the same reactor for the same plasma conditions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1371940]

I. INTRODUCTION

Radio-frequency discharges in low-pressure fluorocarbon gases are widely used for the etching of thin SiO₂ layers in microelectronic circuit fabrication. By careful adjustment of the gas composition (using mixtures of CF₄, C₄F₈, CHF₃, C₂F₆, etc.) it is possible to etch submicron features in SiO₂ with vertical side walls and without etching the underlying silicon layer. In the SiO₂ etching process atomic fluorine plays an important role in forming volatile SiF₂ and SiF₄ etch products, thus removing silicon atoms from the substrate. Simultaneously, C_xF_y fluorocarbon radicals and ions present in the gas phase form a thin polymer layer at the substrate surface, providing carbon atoms to remove the oxygen from the SiO₂ lattice to form COF_x etch products under the influence of energetic ion bombardment. Unfortunately, F atoms can also cause etching of the Si underlayer: the etch is only selective if the discharge deposits a thick enough fluorocarbon polymer film selectively on the Si layer therefore blocking the etching of the latter. In our recent publications,¹⁻³ we have shown that in capacitively coupled discharges, the polymer precursors appear to be high mass ions and/or neutrals formed in the gas phase by radical-radical recombination reactions. Atomic fluorine plays a major role in limiting the formation of these species, so it is important to develop a simple and reliable method to measure its concentration. A number of techniques have been developed in the past but are either difficult to put on an absolute scale or are cumbersome and require sophisticated equipment.

The oldest and most widely used technique for monitoring fluorine atom concentrations in plasmas is optical emission actinometry, originally proposed by Coburn and Chen,⁴ to monitor *relative* variations of the F atom concentration. In this technique relative variations in ground state fluorine atom concentration, $[F]$ are assumed to be proportional to the relative variations in the intensity of the optical emission, I_F , from excited state F atoms, normalized to the optical emission intensity I_{Ar} resulting from the excitation of an actinometer gas such as Ar (introduced in small concentration, $[\text{Ar}]$), so as to correct for electron density and temperature variations. The technique is valid provided that: (1) the optical emission is only produced by direct electron impact excitation of the atoms in each case and (2) the ratio of the excitation rates of both atoms remains constant, i.e.,

$$[F] = [\text{Ar}] \frac{K_{\text{exc}}^{\text{Ar}} I_F}{K_{\text{exc}}^{\text{F}} I_{\text{Ar}}} = K [\text{Ar}] \frac{I_F}{I_{\text{Ar}}}. \quad (1)$$

The validity of this technique in relatively high pressure (300 mTorr) CF₄/O₂ capacitively coupled discharges has been confirmed by titration.^{5,6}

If the value of K is known (either by calculation⁷ or calibration) actinometry should also, in principle, allow absolute concentrations to be determined. In practice, K is not a universal constant: as the electron impact cross sections for the two relevant excitation processes have somewhat different energy dependencies, K depends on the electron energy distribution function (EEDF), which can vary significantly as a function of the plasma pressure, composition, or injected power. In particular, severe difficulties have been encoun-

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tered at low pressure (typically 1 mTorr).⁸ A more detailed discussion of this point will be given in Sec. III.

Absolute fluorine atom concentrations can, in principle, be determined from the resonance absorption at 95 nm, although the absence of any transparent window materials at this wavelength makes this difficult. However, Sasaki *et al.*⁹ have used the UV light generated by a compact plasma discharge in CF₄ to measure the 95 nm resonant absorption in a helicon source. In this technique uncertainty arises from the need to know the spectral profiles of both the source and the absorber, and the technique has a limited dynamic range. However, they estimated that their results were reliable to within 50%. Furthermore, they followed F atom kinetics with time resolution.^{10,11} Subsequently, Kawai *et al.*¹² used resonance absorption to test fluorine actinometry in a helicon source. They showed that for a given working gas relative actinometry measurements are reliable to within a factor of 2 as the rf power is varied, but that the absolute value of K [see Eq. (1)] depends strongly on the feedstock gas used.

Tachibana and Kamisugi¹³ have probed the resonance transition using VUV laser absorption spectroscopy. Frequency mixing techniques were used to produce a spectrally narrow laser beam around 95 nm, which could be tuned over the absorption line profile, allowing the background absorption signal from other plasma species to be subtracted. However, a complex laser system is needed, and it is also possible that saturation of the absorption can occur when using a spectrally sharp laser to excite a strong atomic transition: this could lead to underestimation of the concentration. Herring *et al.*¹⁴ have performed two photon laser induced fluorescence of fluorine atoms at 175 nm. Unfortunately, this method does not give absolute values directly, and has not been applied so far to *in situ* plasma conditions due to its low sensitivity.

Finally, threshold ionization mass spectroscopy has been used to determine absolute fluorine concentrations in CF₄ discharges.^{15–17} However, the signal from atomic fluorine is very weak, and reliable absolute calibration is problematic. Generally the measurements are put on an absolute scale by calibration against the F⁺ signal produced by dissociative ionization of a stable molecule (e.g., CF₄), given knowledge of the relative electron impact cross sections. However, recent work has shown that this can give results that are false by orders of magnitude due to the dependence of the mass spectrometer transmission on the kinetic energy of the dissociative ionization products.¹⁸ Furthermore, desorption of F atoms physisorbed on the walls inside the mass spectrometer can lead to errors unless multistage differential pumping and beam chopping are used.¹⁹

In the present article we report on a simple technique to determine the absolute fluorine atom concentration in a capacitively coupled discharge in pure CF₄. The technique can only be applied to particular plasma conditions, that is to say pure CF₄ plasmas with a low degree of dissociation. However, it has the advantage of being straightforward and reliable in this particular system. The results, presented in Sec. IV, are in reasonable agreement with the literature.

II. TECHNIQUE

The technique is based on the determination of the rate of loss of the CF₂ radical in the afterglow due to the gas-phase recombination reaction



As the rate constant for this reaction is known,²⁰ the fluorine atom concentration can be deduced. However, CF₂ can also be lost by other processes, notably wall-catalyzed recombination, so the rate of loss due to reaction (2) must be separated from these. After the first few milliseconds of the afterglow (during which the concentration profile collapses to the fundamental diffusion mode²¹) the CF₂ concentration decays exponentially with time

$$[\text{CF}_2] = [\text{CF}_2]_0 e^{-k_{\text{loss}} t}. \quad (3)$$

The first order decay rate constant k_{loss} can be expressed as

$$k_{\text{loss}} = k_{\text{gas}} + k_{\text{wall}}. \quad (4)$$

Here k_{gas} represents the sum of all gas-phase reaction rates and k_{wall} represents the diffusive loss to the walls of the reactor, where CF₂ is destroyed by surface-catalyzed recombination. In an oblate cylindrical reactor k_{wall} is mostly determined by axial diffusion to the parallel powered and grounded electrode surfaces. The surface recombination coefficients at each surface, β_1 and β_2 , can be determined from the axial concentration profile at a fixed time in the afterglow,²² and the loss rate due to axial diffusion can then be estimated with knowledge of the diffusion coefficient. If the CF₂ concentration is not perfectly homogeneous across the radius (due, for example, to plasma density inhomogeneity) there can, in addition, be loss due to radial diffusion. However, if the electrode spacing is small compared to the electrode radius, this term will be small.

If the only gas-phase reaction consuming CF₂ is reaction (2) (see discussion below), then we have

$$k_{\text{gas}} = k_{\text{rec}}[\text{F}], \quad (5)$$

where the rate constant $k_{\text{rec}} = 1.8 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$ (from Ryan and Plumb²⁰ and corrected for a bath gas pressure of 200 mTorr CF₄) with an uncertainty of $\pm 15\%$. From Eqs. (1), (4), and (5), we obtain

$$k_{\text{loss}} = k_{\text{wall}} + k_{\text{rec}} K [\text{Ar}] \frac{I_{\text{F}}}{I_{\text{Ar}}}. \quad (6)$$

The total CF₂ loss rate k_{loss} , and the actinometric ratio $I_{\text{F}}/I_{\text{Ar}}$ are then measured as a function of the rf power. Assuming that K , k_{wall} and k_{rad} are independent of the rf power (see discussion below), a plot of k_{loss} against $I_{\text{F}}/I_{\text{Ar}}$ will be linear, with a slope s given by

$$s = k_{\text{rec}} K [\text{Ar}] \quad (7)$$

allowing the F atom density to be determined from Eqs. (1) and (7)

$$[\text{F}] = \frac{s}{k_{\text{rec}}} \frac{I_{\text{F}}}{I_{\text{Ar}}}. \quad (8)$$

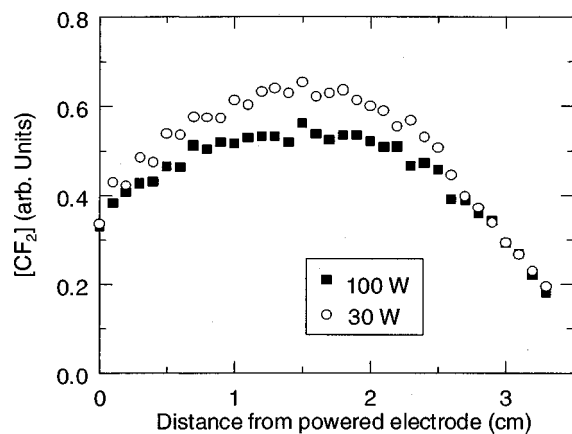


FIG. 1. Concentration profiles of the CF_2 radicals recorded 3 ms in the afterglow of 30 and 100 W plasmas. The concentration gradients near the walls (at 0 and 3.3 cm) are independent of the rf power used during the rf on period, indicating that the surface loss probability of CF_2 in the afterglow is independent of the rf power.

The proportionality constant K can also be determined from the slope s and $[\text{Ar}]$ [from Eq. (7)]. It should be noted that, although the determination of the absolute value of the constant K depends on absolute values for I_F/I_{Ar} (i.e., on accurate knowledge of the wavelength sensitivity of the detection system) and of the Ar gas density, these two quantities factor out in the determination of $[\text{F}]$ for a given reactor and detector system. Therefore, the absolute F atom concentration depends only on k_{rec} and $s \times I_F/I_{\text{Ar}}$ (an error in the wavelength sensitivity of the detectivity will have an inverse effect on s and on I_F/I_{Ar} , and will factor out).

We shall now discuss the four major assumptions upon which this technique reposes.

(1) There must be no significant gas-phase reaction consuming CF_2 except reaction (4). Plumb and Ryan^{20,23} have investigated the possible reactions that can occur in CF_4 plasmas. In low pressure fluorine-rich conditions with pure CF_4 feedstock gas the concentration of CF_x radicals is kept low by gas-phase and surface recombination with fluorine.¹ Therefore reactions of CF_2 with these species (especially CF_3) will be insignificant. Furthermore, the concentrations of oligomeric C_xF_y species is kept low.^{2,3} The rate constant for the reaction of CF_2 with molecular F_2 , (which may well be present in significant concentration under these conditions) is very small (less than $2 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$).²⁰ In the absence of any impurities (for example, oxygen) this assumption is therefore reasonable.

(2) The fluorine atom concentration $[\text{F}]$ must be in excess of $[\text{CF}_2]$, so that its concentration does not vary during the decay rate measurement. The absolute CF_2 concentration has been measured under the same conditions by UV absorption²⁴ (and is of the order of $5 \times 10^{12} \text{ cm}^{-3}$), so this assumption can be verified *a posteriori*.

(3) The diffusion loss rate k_{wall} must be independent of the rf power injected. The surface loss probability of CF_2 on the powered and grounded electrodes can be determined from the axial concentration profiles of CF_2 in the afterglow of a pulsed discharge. The profiles are shown in Fig. 1, for discharges at rf powers of 30 and 100 W. The surface loss

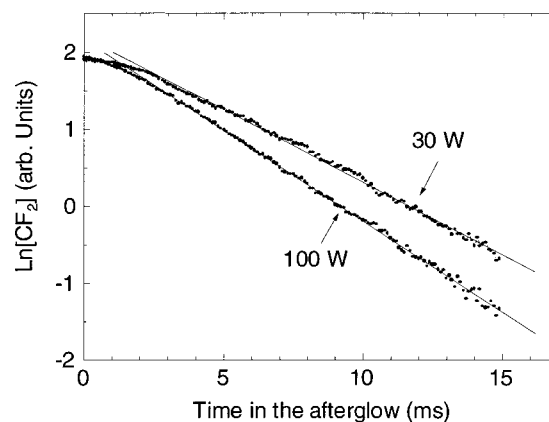


FIG. 2. Logarithm of the CF_2 radical concentration as a function of time in the afterglow of a 200 mTorr, 100 W plasma at 30 and 100 W, together with the exponential fit used to deduce the radical loss rates.

probability β is inversely proportional to the length λ , defined as the intersection of the linear extrapolation of the profile beyond the wall at the concentration=0 axis.²¹ Figure 1 shows that the values of λ on both the powered and the grounded counterelectrode are independent of the rf power to better than 10%, validating our hypothesis. That β does not depend on the rf power is initially somewhat surprising. However, most of the radicals lost on the walls are *not* incorporated into a polymer film (there is almost no polymer deposition in a pure CF_4 plasma) but are directly recycled into the gas phase in the form of CF_4 . As a consequence, the surface loss probability is expected to depend mostly on the density of F atoms available at the surface. In a fluorine-rich plasma the surface will become quickly saturated in F atoms in the absence of ion bombardment so that the surface loss probability *in the afterglow* is independent of the rf power, explaining our observation. This assumption also depends upon the value of the diffusion coefficient being constant, which means that the gas temperature must be constant in time and uniform across the reactor. Whereas this assumption has been shown to be reasonable in low-density capacitively coupled plasmas,²⁵ it is clearly not the case in higher-density inductively coupled plasmas, where significant gas heating can occur.²⁶

(4) Actinometry must be a reliable indicator of the relative change in the F atom density. First, the value of the actinometry proportionality constant K must not vary, at least over the parameter range explored in this study.

The value of K is given by

$$K = \int_0^{\infty} \sigma_{\text{Ar}}(\epsilon) \sqrt{\epsilon} f(\epsilon) d\epsilon / \int_0^{\infty} \sigma_{\text{F}}(\epsilon) \sqrt{\epsilon} f(\epsilon) d\epsilon. \quad (9)$$

In Eq. (9), $\sigma_{\text{F}}(\epsilon)$ and $\sigma_{\text{Ar}}(\epsilon)$ denote the excitation cross sections of F and Ar atoms by electron impact to their ground state (at energy ϵ), and $f(\epsilon)$ is the EEDF. The threshold and cross sections of Ar and F atoms are slightly different which implies that K is dependant on the EEDF shape. However, experiments by Kawai *et al.*¹² in a helicon plasma source have shown that, although the value of K depends

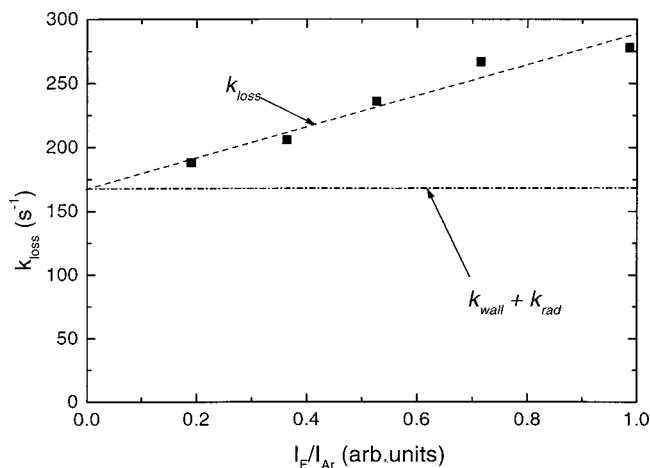


FIG. 3. CF_2 loss rate as a function of the actinometric ratio $I_{\text{F}}/I_{\text{Ar}}$. The value of this ratio was varied by changing the rf power from 30 to 150 W. The dash-dot line indicates the constant loss rate due to diffusion to the reactor walls, $k_{\text{wall}} = 170 \text{ s}^{-1}$.

somewhat on the feedstock gas, actinometry measurements are fairly reliable for a given gas unless the mode of the discharge regime changes from E (capacitive) to H (inductive) to W (wave sustained), i.e., unless there is an important change in the EEDF shape induced by a heating mode transition or a change in the gas-phase chemistry. In our experiment, we use actinometry to deduce the relative variation of $[\text{F}]$ for very similar plasma conditions (same parent gas, same pressure, pure capacitive discharge), and we assume that the power variation is small enough to keep roughly the same EEDF shape for both conditions.

Second, the excited states of the F and Ar atoms that produce the observed optical emission must be populated only by electron impact from the ground state atoms (and not by dissociative excitation of the feedstock gas, or by multi-step excitation). Hancock *et al.*²⁷ have shown that dissociative excitation can become a significant proportion of the actinometry signal in fluorine-poor plasmas, for example when CHF_3 feedstock is used, when the process:



becomes important. However, this assumption appears to be reasonable in fluorine-rich conditions.

III. EXPERIMENT

The experimental setup and apparatus used in this experiment has been described in detail elsewhere.²² The plasma reactor is a typical 30 cm diameter reactive ion etching chamber composed entirely of aluminum. The 11 cm diameter powered electrode, fed with rf power at 13.56 MHz, is surrounded by a coplanar annulus, and is faced by a grounded electrode that is parallel to both surfaces with a spacing of 3.3 cm. Fused silica windows in the reactor side walls allow the passage of the laser beam and the detection of induced fluorescence.

All experiments were carried out at a discharge pressure of 200 mTorr of CF_4 gas with 5 mTorr of Argon added as the actinometer. The discharge power was 100% modulated at 10 Hz (80 ms on/20 ms off) in order to perform time-resolved measurements in the afterglow. The CF_2 radical was detected by laser-induced fluorescence (LIF) using an excimer-pumped dye laser system with frequency doubling to produce pulsed radiation at 234 nm.¹ The axial concentration profiles of CF_2 between the electrodes were obtained at arbitrary times during the on/off cycle by translation of the reactor relative to the LIF optics.^{1,22} The decay rate k_{loss} of the CF_2 concentration in the afterglow was measured in the center of the chamber by monitoring the LIF signal as a function of time in the afterglow at this position and fitting the logarithm of the data. Simultaneously, the optical emission from fluorine (703.7 nm) and argon (750.4 nm) atoms was monitored using a 60 cm Jobin–Yvon monochromator, equipped with a Hamamatsu 928 photomultiplier. The optical emission intensities were corrected for the wavelength dependence of the detectivity.

IV. RESULTS AND DISCUSSION

In the following discussion, the term “fluorine rich” refers to measurements in a pure CF_4 plasma, without a wafer being etched in the reactor, whereas the term “fluorine-poor” refers to measurements in a CF_4 plasma with Si or SiO_2 wafers on the powered electrode.

A. Fluorine-rich plasma conditions

The time variation of the natural logarithm of $[\text{CF}_2]$ in the afterglow for two discharge powers (30 and 100 W) is shown in Fig. 2. In both cases the decay is single exponential after the first few milliseconds of the afterglow, and the slope (in the log scale) can be determined accurately. The nonexponential decay during the first 2 ms of the afterglow is due to the relaxation of higher order diffusion modes (we measure the concentration in the middle of the cell, but the highest concentration in the steady state plasma is adjacent to the powered electrode).¹ Thus k_{loss} was obtained by fitting the exponential part of the decay, ignoring the first 2 ms. The single exponential decay shows that wall losses (k_{wall}) and radial diffusion losses (k_{rad}) do not change during the after-

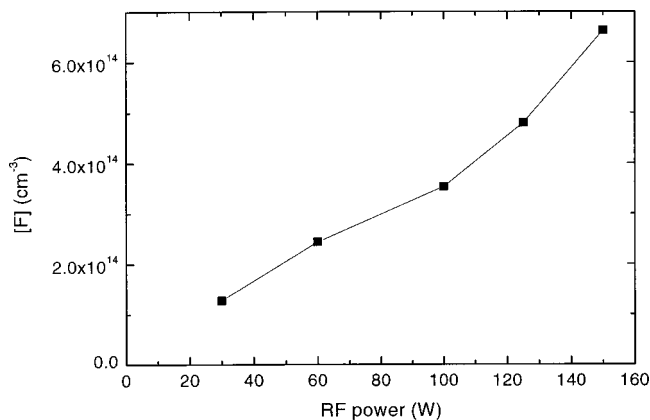


FIG. 4. Fluorine atom concentration as a function of rf power for a CF_4 plasma at 200 mTorr and without a substrate in the reactor.

TABLE I. Absolute fluorine atom concentration in CF₄ plasmas, in units of 10¹⁴ cm⁻³, for various discharge conditions and etched substrates.

Pressure (mTorr)	Power (W)	[F] (10 ¹⁴ cm ⁻³)		
		Al (no substrate)	SiO ₂ (substrate)	Si (substrate)
50	30	0.3	0.29	0.15
	100	1.8	1	0.5
200	30	1.3	1.2	1.1
	100	3.6	3.4	1.5

glow. It also demonstrates that volume recombination with species in small concentrations (for example CF₂+CF₂ or CF+CF₂) is unlikely. The increased decay rate observed at higher discharge power can therefore be attributed to the increased F atom concentration due to higher dissociation degree of the parent gas.

Figure 3 shows k_{loss} as a function of the actinometric ratio $I_{\text{F}}/I_{\text{Ar}}$. The value of this ratio was varied by varying the rf power from 30 to 150 W. The curve in Fig. 3 is linear, which is a strong justification of the validity of the technique. It demonstrates that wall losses (k_{wall}), radial diffusion losses (k_{rad}) and the ratio of excitation coefficient K do not change significantly with the rf power [point (3) and (4) of paragraph 3]. From slope of the line [see Eq. (7)] we find a value of 4.1 for the parameter K . This is very similar to that deduced experimentally ($K=4.3$) by Kawai *et al.*¹² in a CF₄ helicon plasma operating at low power, similar to our capacitively coupled plasma. However, it is 7 times higher than the value ($K=0.56$) calculated by Jeng *et al.*⁷ from excitation cross-section data. Finally, the extrapolation at $I_{\text{F}}/I_{\text{Ar}}=0$ of the line Fig. 3 gives a value for $k_{\text{wall}}+k_{\text{rad}}=170 \text{ s}^{-1}$ (see Fig. 3). This shows that CF₂ volume losses represent only 10% of the total losses at 30 W, but become significant (about 40% of the total losses) at 150 W.

Figure 4 shows the fluorine atom concentration as a function of rf power, deduced from Eq. (8). As expected, the fluorine atom concentration increases with rf power. It should also be noted that the value of [F] increases monotonically throughout this power range, which shows that the plasma is far from being fully dissociated. At 150 W, [F] = $6.6 \times 10^{14} \text{ cm}^{-3}$ which corresponds to a partial pressure of 20 mTorr (the CF₄ pressure when the plasma is off is 200 mTorr).

B. Extrapolation to fluorine-poor plasma conditions

The absolute F atom concentration for the various combinations of plasma parameters corresponding to the plasma conditions described in Refs. 1 and 2 are listed in Table I, completing the data on CF_x radicals in CF₄ discharges. The relative F atom concentrations were obtained from relative actinometry and put on an absolute scale using the value determined in an empty reactor at 200 mTorr/100 W ([F] = $3.6 \times 10^{14} \text{ cm}^{-3}$). Unfortunately, a direct measure under fluorine-poor conditions (when a substrate is etched) is not possible since additional CF₂ loss processes become important.²

As expected, the results show that the fluorine atom concentration is lower when a substrate is etched (loading effect). The lowest value of $1.5 \times 10^{13} \text{ cm}^{-3}$ is obtained at low power and low pressure when a silicon substrate is etched. It seems that the absolute F concentration at 200 mTorr during the etching of a Si substrate (fluorine-poor conditions since the silicon depletes the F concentration by forming SiF_x species) is about $1.5 \times 10^{14} \text{ cm}^{-3}$, that is only 2.4 times lower than without substrate. This suggests that the spectacular change that occurs in the plasma chemistry when a Si substrate is introduced^{1,2} is caused by a fairly small change in the F atom concentration. Nevertheless, it is impossible to rule out the possibility of a significant contribution to the fluorine actinometry signal by dissociative excitation of the feedstock gas under fluorine-poor conditions, which would result in overestimation of the fluorine atom concentrations.

V. CONCLUSION

The absolute concentration of F atoms has been measured in a pure CF₄ capacitively coupled plasma using a technique based on CF₂ loss kinetics. This approach can be used in fluorocarbon plasmas under F-rich conditions when the dominant chemical reaction consuming CF₂ radicals is recombination with F atoms, and when wall and radial diffusion losses are independent of rf power. Under these specific conditions, we estimate that the results are reliable to within 50%, equivalent to the uncertainty of other techniques such as VUV absorption.

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