# Laser-induced fluorescence of CF and $CF_2$ radicals: an *in-situ* diagnostic for polymer treatment in $CF_4$ discharges

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**Abstract:** LIF and actinometry were used to monitor the temporal evolution of $CF_2$ and F in $CF_4$ and $CF_4/H_2$ plasmas in the presence of a hydrocarbon polymer surface. The surface consumes both species and becomes passivated over a timescale of ~100 s. The wettability of polymer surfaces treated by $CF_4$, $CF_4/H_2$ and $F_2/He$ discharges was measured. Whereas the wettability was increased by $F_2/He$ treatment, the lowest wettabilities were achieved in the F-deficient, $CF_2$-rich $CF_4/H_2$ mixtures.

## I. Introduction

Tetrafluoromethane plasmas have been successfully employed in the processing of microelectronic materials, the fabrication of thin polymer films, and the treatment of polymer surfaces. Fluorocarbon plasma treatment of polymers leads to modification of surface properties by fluorination [1], which may occur by two mechanisms: functionalization [2] and polymerization [3]. A decrease of the surface wettability, following exposure of the polymer to the discharge, is then obtained to a degree depending on the treatment time and the composition of the gas mixture [4-6].

To achieve a better understanding of the role of the most abundant reactive plasma species, namely the F atoms and the fluorocarbon radicals CF, $CF_2$ and $CF_3$, *in-situ* diagnostics have been developed such as threshold ionization mass spectrometry [7,8], UV absorption spectroscopy [9], infrared diode laser absorption spectroscopy [10], and optical emission spectroscopy [11,12] which has been widely employed during polymer treatment in $CF_4$ discharges [13,14]. Laser-based diagnostics are ideal to monitor radical concentrations due to their ability to detect ground state radical species with excellent spatial resolution. Laser-induced fluorescence (LIF) is a well-established technique that has been employed to monitor CF and $CF_2$ concentrations, spatially and temporally resolved [15,16]. In this work, LIF is used for the first time in order to probe the concentration of CF and $CF_2$ during the treatment of a polymer surface in a reactive ion etching reactor (RIE) and a flowing afterglow microwave reactor. The temporal evolution of these species is correlated to the simultaneous modification of the polymer surface properties investigated by *ex-situ* XPS and surface energy measurements. Finally, in order to further elucidate the role of the various radicals, different gas mixtures, such as $CF_4/H_2$ at various compositions and $F_2/He$, were employed and their effect on the surface modification was investigated.

Hexatriacontane (HTC) was used as a model molecule of high-density polyethylene, since it provides a better defined polymer surface exhibiting the same behavior as that of the corresponding polymer under plasma treatment [4].

## II. Experimental

Experiments were carried out in two reactors; a modified Nextral RIE reactor and a homemade flowing afterglow microwave reactor. In the RIE reactor, the discharge was created by supplying rf power (30-150 W, 13.56 MHz) to a 10-cm-diam lower electrode separated by 3 cm from a 8-cm-diam grounded electrode, both made of aluminum. The polymer sample to be treated was placed on the grounded electrode and it was of the same diameter. In the microwave reactor, the plasma was produced by an air-cooled Evenson microwave cavity in a pyrex tube passed through the cavity and it extended over the full length of the tube (15 cm). The power was kept constant at 50 W. Flow rates for the gases introduced in the reactors were measured by MKS flowmeters and the pressure, measured by a MKS capacitance manometer, was adjusted to values between 50 and 200 mTorr. The polymer sample was placed on a movable holder and was positioned approximately 2 cm downstream of the edge of the visible plasma volume, in the discharge afterglow. Both reactors were fitted with UV grade windows, that allowed UV laser excitation of the radical species a few mm away from the polymer surface and collection of the UV fluorescence at right angles with respect to the laser beam.

The radicals CF and $CF_2$ were detected by LIF. Excitation of the ground state was accomplished with a pulsed tunable laser system; a Lambda Physik excimer laser was used to pump a LPD3000 dye laser operating with Coumarin 47 dye and a BBO frequency doubling crystal. The $CF_2$ radical was detected by excitation of the $\tilde{A}(0,11,0)$-$\tilde{X}(0,0,0)$ band at 234.3 nm with observation of the fluorescence at 248.5 nm to the $\tilde{X}(0,4,0)$ level, while the CF radical was detected by excitation of the $\tilde{A}$-$\tilde{X}$ (1,0) band at 223.8 nm with observation of the (1,1) fluorescence at 230.6 nm. The fluorescence was collected by a UV grade quartz lens and it was imaged onto a 20 cm monochromator, the output of which was viewed by a Hamamatsu R3896 photomultiplier tube (PMT). The signal of the PMT was integrated over the fluorescence lifetime with a boxcar integrator (Stanford Research SR250) and recorded on a personal computer via a A/D converter.

To examine the surface modification, two *ex-situ* complementary measurements were realized. First, the contact angles of distilled water and glycerol (volume 2 µl) were measured on the polymer surface and the surface energy was then calculated from the Young-Dupré relation [17]. Second, XPS measurements were performed at CNS-CNET (Grenoble, France).

## III. Results and Discussion

The CF and $CF_2$ radicals were detected in the RIE reactor and in the flowing afterglow of a microwave reactor. Since the temporal evolution of $CF_2$ in the presence of an untreated HTC sample was similar in both reactors, only the results obtained in the microwave discharge will be presented here. Supplied with a movable substrate holder, the microwave reactor permitted the direct comparison of radical concentrations in the presence and in the absence of a polymer sample in the same discharge. The CF radicals detected in the RIE reactor followed the general trend of $CF_2$ that will be presented below. Surprisingly, no CF radicals were detected in the discharge afterglow (in contrast to RIE reactor [16]), probably due to both, a low production rate from $CF_4$ due to the low electron energy that characterizes microwave discharges, and the short lifetime of CF radicals as opposed to that of $CF_2$ [16,18].

The observed evolution of $CF_2$ radicals in the flowing afterglow reactor is shown in Fig. 1, for a pressure of 200 mTorr of pure $CF_4$, in the presence of initially untreated and treated polymer samples. The discharge was turned on (t=0 sec) with the polymer already placed at the edge of the visible plasma volume. The transient behavior of

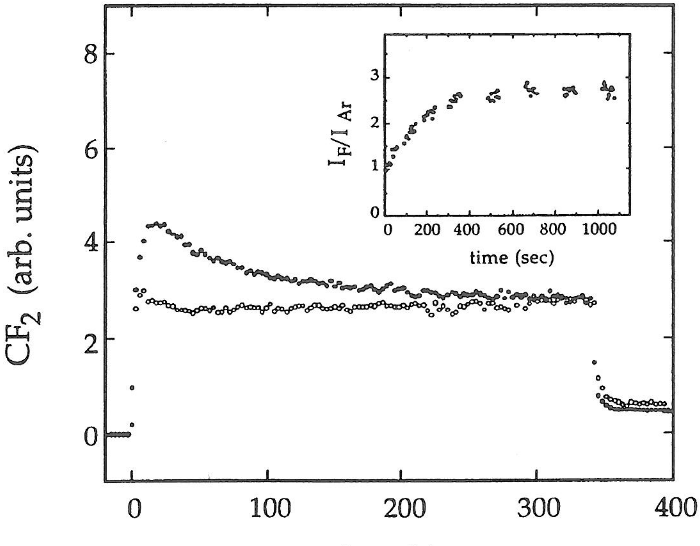

Figure 1. Evolution of $CF_2$ radicals in the presence of an initially untreated (filled circle) and a treated (open circle) HTC sample in a pure $CF_4$ discharge (plasma on at t=0 s, HTC removed at t=340 s). Discharge conditions: 50 W, 200 mTorr. Inset: Evolution of F obtained by actinometry.

$CF_2$ is characterized by an initial increase in concentration during the first 10's seconds, followed by a decay to a steady state value, after a few minutes, which is similar to that of a treated sample. The evolution of $CF_2$ is strikingly different from that of F atoms which, as we observed by actinometry (inset of Fig. 1) and in agreement with previous work [13], increases monotonically. This suggests that the HTC surface initially consumes F atoms. When the sample is removed from the probed region (at t=340 sec) the concentration of $CF_2$ is significantly reduced, indicating a suppression of $CF_2$ losses in the presence of HTC. This could be attributed to surface recombination of F atoms on the passivated HTC, which would reduce the F atom concentration in gas phase and hence reduce the loss of $CF_2$ by both gas-phase recombination with F and/or surface removal [19,20]. To determine the exact nature of the loss mechanism, the $CF_2$ kinetics in a pulsed discharge will be examined in the near future.

The modification of the surface probed by contact angle measurements on HTC samples showed that surface energy decreases sharply even after a brief exposure of HTC to the discharge and levels out for treatments longer than 3 min. Thus, the modification of the surface energy correlates well with the temporal evolution of $CF_2$ radicals, verifying that the LIF technique can be used as a means for end-point control of polymer surface fluorination in a $CF_4$ plasma.

By varying the gas composition in the feed, we could change the relative concentration of active species (F, $CF_2$, $CF_3$), and thus modify the kinetics of the discharge. The general trend observed for the $CF_2$ temporal evolution in a pure $CF_4$ discharge changed drastically upon addition of $H_2$, a fluorine reducing agent. This is shown in Fig. 2, where a 15% $H_2$ was added to the $CF_4$ discharge. In this case, an exponential *increase* with time was observed for $CF_2$ radicals. Measurements of the steady-state $CF_2$ concentration as a function of the percentage of $H_2$ added in the discharge (inset of Fig. 2) further indicate that the concentration of $CF_2$ reached a maximum at about 15% of $H_2$ added in the feed. This effect has been observed previously in rf discharges [19,20] and was attributed to greatly decreased surface loss for $CF_2$ upon the addition of $H_2$. The HTC surface is now the dominant loss surface for $CF_2$, until it too becomes passivated by polymer deposition.

The polymerizing system $CF_4/H_2$ has been investigated in detail in the past [6,19,20,21]. It has been shown that by introduction of a reducing agent, such as $H_2$, a drastic reduction of F atoms occurs, and an increase in $CF_x$ radical concentration. This behavior was explained by reactions between F and $H_2$ leading to a reduction in F atom concentration in gas phase and an increase in polymer deposition on the reactor surfaces, thus being responsible for a decrease in gas-phase and/or surface losses of $CF_2$. Our observations suggest that, at the point where the concentration of $CF_2$ is at a maximum, the polymer surface is passivated predominantly by $CF_2$ radicals.

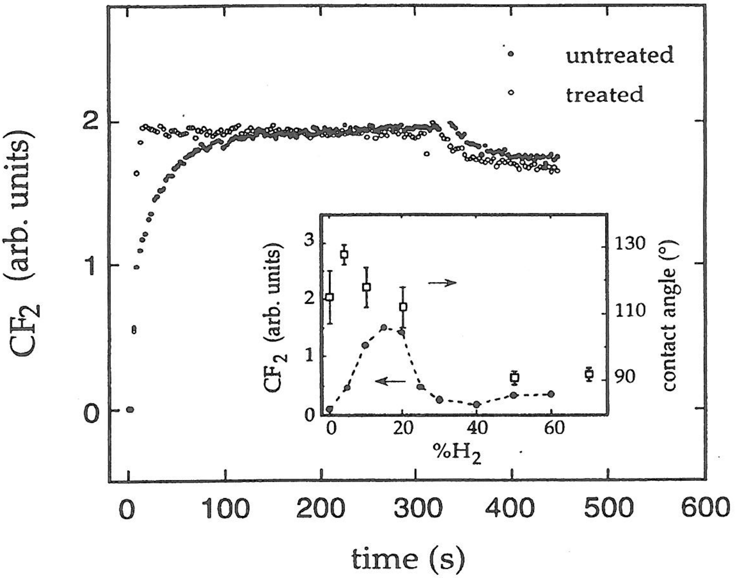

Figure 2. Evolution of $CF_2$ radicals in the presence of an initially untreated (filled circle) and a treated (open circle) HTC sample, in a 15% $H_2/CF_4$ discharge (plasma on at t=0 s, HTC removed at t=340 s). Inset: $CF_2$ concentration and contact angle (after a 2 min treatment) as a function of the percentage of $H_2$ added in the feed. Discharge conditions: 50 W, 100 mTorr.

Measurements of the contact angle of HTC treated in $H_2/CF_4$ mixtures showed that the maximum contact angle was achieved at a small percentage of $H_2$ added to $CF_4$ (inset of Fig. 2), in agreement with previous work [6]. Although this mixture does not coincide exactly with that at which the concentration of $CF_2$ was found to be at maximum, the result however indicates that a more hydrophobic surface is obtained when the concentration of atomic fluorine is considerably reduced. This can be explained since F atoms are known to be etching agents, while $CF_2$ radicals act as polymer building blocks [21]. When a discharge rich in atomic fluorine was used ($F_2$/He), the contact angle was found significantly reduced, to an even lower value than that corresponding to an untreated HTC surface, suggesting that the role of $CF_2$ and/or $CF_3$ to the decrease of the surface wettability is quite indispensible.

In conclusion, we have shown that the concentration of $CF_2$ detected through LIF provides a means of monitoring the surface modification which can be observed independently by *ex-situ* surface analysis. The initial enhancement of $CF_2$ in a pure $CF_4$ discharge is consistent with a consumption of atomic fluorine on the HTC surface. $CF_2$ radicals exhibit surface-dominated losses on the initially untreated polymer only when atomic fluorine is drastically reduced with addition of a small percentage of $H_2$ in the feed. Furthermore, the role of $CF_2$ and/or $CF_3$ to the decrease of the surface wettability appears to be quite important; the wettability is minimum in a discharge deficient in atomic fluorine ($H_2/CF_4$), while it increases in the absence of $CF_2$ ($F_2$/He discharge). It remains to be shown whether this reduced wettability is due to substitution of H atoms by $CF_x$ radicals, or due to deposition of fluorinated polymers on the HTC surface.

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