Detection of CF_2 radicals in a plasma etching reactor by laser-induced fluorescence spectroscopy

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(Received 7 December 1981; accepted for publication 24 February 1982)

Laser-induced fluorescence spectroscopy was used to detect ground-state CF_2 radicals in 13.56-MHz discharge plasmas sustained in C_2F_6 and CF_4 in a plasma etching reactor. Measurements of the relative $CF_2(\tilde{X})$ density in each plasma as a function of discharge power demonstrated that CF_2 densities were significantly higher in the C_2F_6 plasma. These results provide the first direct observation of $CF_2(\tilde{X})$ radicals in a plasma etching reactor.

PACS numbers: 82.30.Cf, 32.50. + d, 52.80.Pi, 52.25.Ps

In this letter we report on the application of laser-based diagnostics to the study of the plasma etching process. Laser-induced fluorescence spectroscopy was used to measure the relative concentration of CF_2 radicals in fluorocarbon plasmas which are used to etch semiconductor devices. Previous studies of plasma etching processes have used optical emission spectroscopy to identify a number of important species in plasma etching reactors[1–6] and to develop endpoint monitors for process control.[2,3,7–11] Optical emission data has also been used for the interpretation of kinetic mechanisms in plasma etching reactors.[4–6] However, the use of such data is suspect because (1) the excitation rate from the ground state to the observed excited state is often unknown and may depend on external parameters such as gas pressure and flow rate,[12] and (2) the lack of spatial resolution restricts one to line-of-sight measurements which provide little information about the important gas-surface interface region. These limitations are overcome by the use of laser-induced fluorescence spectroscopy since ground-state concentrations are measured directly and the technique inherently possesses high spatial resolution. In addition, in most cases the technique can be considered a nonperturbative probe.

Initial experiments were carried out in a static gas cell to obtain the spectroscopic data required for the quantitative detection of CF_2 radicals. A high steady-state concentration of CF_2 radicals for these studies was obtained by using a neodymium-yttrium aluminum garnet (YAG) laser (Quanta-Ray DCR-1), which was frequency quadrupled to 266.0 nm as the photolysis source for the multiphoton photodissociation of C_2F_6.[13] A schematic diagram of the apparatus used for this experiment is shown in Fig. 1. The apparatus is similar to the one used for laser Raman spectroscopy in Ref. 14, where it is described in detail. A boxcar integrator (Princeton Applied Research model 162 with model 164 gated integrators) with an output time constant of ~ 1 s was used to average the signal from the photomultiplier tube. For the experiment reported here the stainless-steel gas cell was pumped down to a base pressure of $\sim 5\times 10^{-7}$ Torr and then filled with 5 Torr of C_2F_6. The 266-nm photolysis laser was operated at 10 Hz and its output was focused in the center of the gas cell by an $f/10$ lens with a 25.4-cm focal length. The fluorescence spectrum of the ground-state CF_2 radicals was conveniently excited by a krypton-fluoride (KrF) laser (Lambda-Physics EMG-500), which was operated at 10 Hz and a nominal wavelength of 248.5 nm with a bandwidth of 0.5 nm. The KrF laser output was also focused in the center of the gas cell by a similar lens. The KrF laser pulse was delayed $\sim 10\,\mu$s relative to the 266-nm laser pulse.

To ensure that the observed CF_2 emission was due to the reaction sequence

$$CF_2(\tilde{X}) + h\nu(248\ \text{nm}) \rightarrow CF_2(\tilde{A}),$$
$$CF_2(\tilde{A}) \rightarrow CF_2(\tilde{X}) + h\nu(\text{fluorescence}), \quad (1)$$

the following procedure was followed (see Fig. 2). Excitation spectra were first recorded with each individual laser alone [Figs. 2(a) and 2(b)]. These spectra were recorded with the KrF laser operating at 100 mJ/pulse and the 266-nm, laser operating at 50 mJ/pulse. Our detection limit was improved in each case by using liquid filters to suppress the scattered laser light.[15] Each spectrum shows only the characteristic C_2F_6 Raman lines. With both lasers operating, very strong CF_2 fluorescence[16,17] excited by the 248-nm KrF laser was observed [Fig. 2(c)]. The KrF laser excited the $\tilde{A}$ (0, 6, 0)$\leftarrow\tilde{X}$(0, 0,0) transition in CF_2 at 248.35 nm. For this measurement the KrF laser energy was reduced to 10 mJ/pulse. Nevertheless, the CF_2 peak fluorescence emission at 270.9

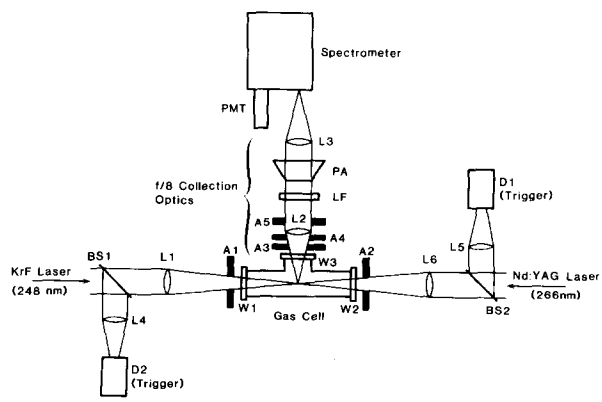

FIG. 1. Schematic diagram of the experimental apparatus showing lenses (L), windows (W), apertures (A), liquid filter (LF), Pechan prism (PA), beam splitters (BS), detection diodes (D), and photomultiplier tube (PMT).

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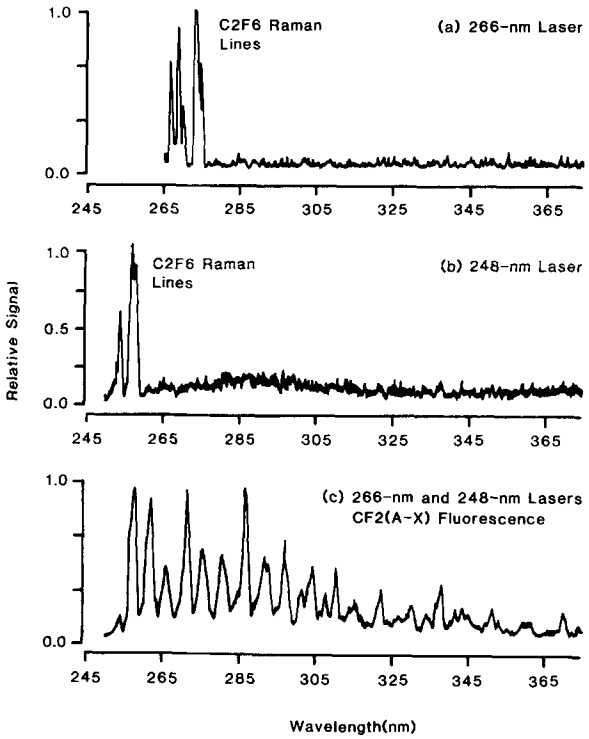

FIG. 2. Emission spectra from 5 Torr C_2F_6 recorded with (a) 266-nm laser excitation, (b) 248-nm laser excitation, and (c) 248-nm laser excitation of CF_2 radicals produced by the 266-nm photodissociation of C_2F_6. Each spectrum is uncorrected for instrument response.

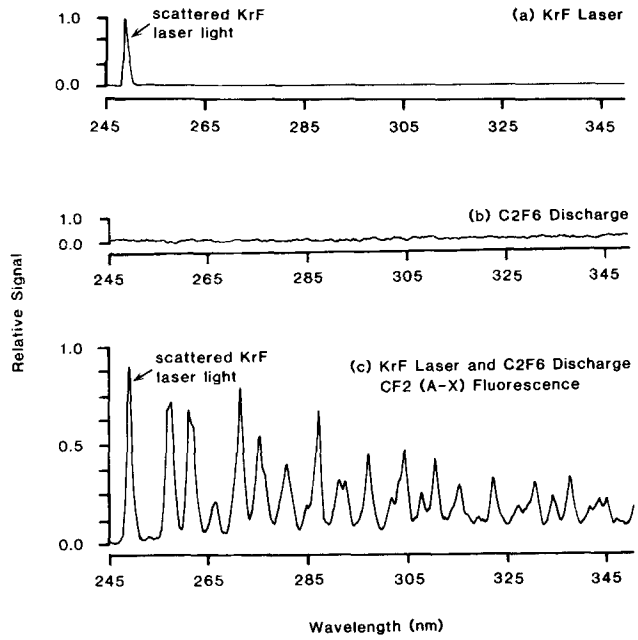

FIG. 3. Emission spectra from 215 mTorr C_2F_6 recorded with (a) 248-nm laser excitation, (b) 13.56-MHz discharge excitation, and (c) 248-nm laser excitation of CF_2 radicals produced by the radiofrequency discharge in C_2F_6. Each spectrum is uncorrected for instrument response.

nm was ~500 times the intensity of the peak Raman signal from C_2F_6. Fluorescence emission originating from the reaction sequence in Eq. (1) was also verified by the long residence time of $CF_2(\tilde{X})$ in the static gas cell, the $CF_2(\tilde{A})$ fluorescence emission lifetime, and the low quenching rate of $CF_2(\tilde{A})$ emission by CF_4 and C_2F_6.

The results presented above demonstrate that $CF_2(\tilde{X})$ radicals are unambiguously detected with KrF laser excitation. Additional results that we have obtained demonstrate that quenching of the $CF_2(\tilde{A})$ fluorescence by CF_4 and C_2F_6 is negligible, especially under plasma etching conditions consisting of total pressures below 200 mTorr.

We applied the technique described above to the detection of $CF_2(\tilde{X})$ radicals in a parallel plate radiofrequency plasma etching reactor. The static gas cell was replaced by a reactor in which a 13.56-MHz discharge could be sustained. The feed gases were flowed at 50 sccm to 100 sccm resulting in a gas change in the reactor every two to three seconds. The aluminum plate electrodes were 10 cm in diameter and were separated by 4 cm. The 266-nm photolysis laser was removed and only the 248-nm KrF probe laser operating at 10 Hz and 10 mJ/pulse was used. The liquid filters used to suppress scattered laser light were also removed. The experimental apparatus otherwise remained the same.

To ensure that the observed CF_2 emission was due only to laser-induced fluorescence from plasma produced radicals, the following procedure was followed (see Fig. 3). The reactor was filled with 215 mTorr of C_2F_6 and the region from 240 to 350 nm was scanned in the absence of the discharge but with the KrF laser radiation focused in the reactor. Only the scattered 248-nm laser light was observed [Fig. 3(a)]. When the discharge was turned on and the laser turned off no emission was observed [Fig. 3(b)] since the gated observation time (50 ns at 10 Hz) was too short to observe any cw plasma emission. When the discharge and KrF laser were simultaneously in operation, strong CF_2 fluorescence identical to that in Fig. 2(c) was observed [Fig. 3(c)]. Similar results were obtained in CF_4. This procedure confirms the observation of plasma produced CF_2 radicals via laser-induced fluorescence in C_2F_6 and CF_4 plasmas.

For purposes of a parametric study, a particularly strong CF_2 fluorescence line, the $\tilde{A}(0, 6, 0) \rightarrow \tilde{X}(0, 5, 0)$ line at 270.9 nm, was selected. The relative $CF_2(\tilde{X})$ density in C_2F_6 and CF_4 plasmas was then measured as a function of discharge power by monitoring the peak laser-induced fluorescence signal at 270.9 nm. For this measurement we have assumed that the relative number of CF_2 radicals in each vibrational level of the ground state is approximately the same for each parent gas. The results in Fig. 4 show that the CF_2 density increases with increasing discharge power. Note also that both the relative CF_2 density and rate of increase in CF_2 density are larger in the C_2F_6 plasma than in the CF_4 plasma. This behavior is expected upon examining the dissociation mechanisms in each plasma.

In C_2F_6, a likely reaction sequence is[18,19]

$$e + C_2F_6 \rightarrow 2CF_3 + e, \qquad (2)$$

$$e + CF_3 \rightarrow CF_2 + F + e,$$

yielding the net reaction

$$C_2F_6 \rightarrow 2CF_2 + 2F. \qquad (3)$$

In CF_4, a likely reaction sequence is[18,19]

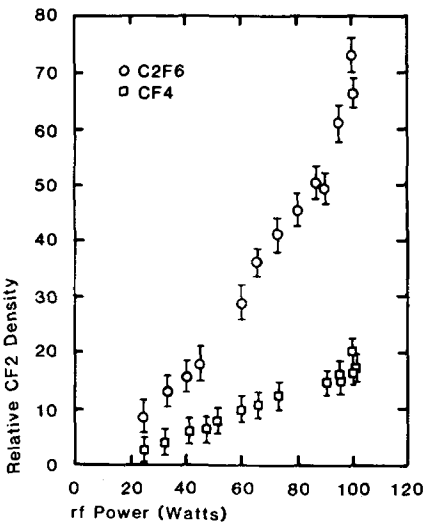

FIG. 4. Relative density of CF_2 radicals in C_2F_6 and CF_4 plasmas recorded as a function of discharge power.

$$e + CF_4 \rightarrow CF_3 + F + e, \tag{4}$$

$$e + CF_3 \rightarrow CF_2 + F + e,$$

yielding the net reaction

$$CF_4 \rightarrow CF_2 + 2F. \tag{5}$$

The net reaction sequences [Eqs. (3) and (5)] show that twice as many CF_2 radicals will be produced from the parent molecule in C_2F_6 plasmas. In addition, the ratio of F atoms to CF_2 radicals is larger in the CF_4 plasma. This means that the reassociation reaction

$$CF_2 + F + M \rightarrow CF_3 + M \tag{6}$$

is more probable in the CF_4 plasma, which further reduces the number of CF_2 radicals in the CF_4 plasma. Our results on the relative abundance of CF_2 radicals in CF_4 and C_2F_6 radiofrequency discharges are consistent with recent measurements of the dissociation cross section of CF_4 and C_2F_6 by electron impact[20] in which the peak cross section for dissociation of C_2F_6 was found to be 1.6 times that for CF_4.

In conclusion, we have demonstrated that CF_2 radicals can be detected by laser-induced fluorescence excited by a KrF laser operating at a wavelength of 248 nm. The technique was used to observe CF_2 radicals in 13.56-MHz discharge plasmas sustained in C_2F_6 and CF_4. We found that for a given discharge power higher CF_2 densities were obtained in C_2F_6 plasmas than in CF_4 plasmas.

The authors would like to acknowledge the expert technical assistance of Mr. A. F. Wright and Mr. J. L. Dishman. This work was supported by the United States Department of Energy.

[1]E. O. Degenkolb, C. J. Mogab, M. R. Goldrick, and J. E. Griffiths, Appl. Spectrosc. **30**, 520 (1976).
[2]W. R. Harshbarger, R. A. Porter, T. A. Miller, and P. Norton, Appl. Spectrosc. **31**, 201 (1977).
[3]B. J. Curtis and H. J. Brunner, J. Electrochem. Soc. **125**, 829 (1978).
[4]C. J. Mogab, A. C. Adams, and D. L. Flamm, J. Appl. Phys. **49**, 3796 (1978).
[5]R. G. Frieser and J. Nogay, Appl. Spectrosc. **34**, 31 (1980).
[6]D. L. Flamm, J. Appl. Phys. **51**, 5688 (1980).
[7]J. E. Griffiths and E. O. Degenkolb, Appl. Spectrosc. **31**, 134 (1977).
[8]B. B. Stafford and G. J. Gorin, Solid State Technol. **20**, 51 (1977).
[9]B. J. Curtis, Solid State Technol. **23**, 129 (1980).
[10]M. Oshmia, Jpn. J. Appl. Phys. **20**, 683 (1981).
[11]P. J. Marcoux and P. D. Fow, Solid State Technol. **24**, 115 (1981).
[12]J. W. Coburn and M. Chen, J. Vac. Sci. Technol. **18**, 353 (1981).
[13]The mechanism for the production of CF_2 radicals from the 266-nm multiphoton photodissociation of C_2F_6 will be presented in a future paper.
[14]P. J. Hargis, Jr., Appl. Opt. **20**, 149 (1981).
[15]A 10-mm path length cell of neat butyl acetate and neat *N,N* dimethylformamide was used to suppress scattered 248- and 266-nm laser light, respectively.
[16]D. S. King, P. K. Schenck, and J. C. Stephenson, J. Molec. Spectrosc. **78**, 1 (1979).
[17]Quach-Tat-Truny, G. Durocher, P. Scuvayeau, and C. Sandorfy, Chem. Phys. Lett. **47**, 404 (1977).
[18]D. L. Flamm, Solid State Technol. **22**, 109 (1979).
[19]E. A. Truesdale and G. Smolinsky, J. Appl. Phys. **50**, 6594 (1979).
[20]H. F. Winters, Phys. Rev. A (to be published).