Glass Etching Initiated by Excimer Laser Photolysis of CF₂Br₂

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KrF and ArF excimer laser irradiation of glass surfaces immersed in gaseous CF_2Br_2 is found to induce etching. The etch mechanism is considered to be nonthermal on the basis of the small value of the glass absorption coefficient and wavelength variable etching experiments. The etch rate dependence on surface fluence is presented for three pressures. SEM photos reveal a rough surface morphology in the etched region that apparently is not a chemical effect but results solely from the laser irradiation. Photochemical and spectroscopic analysis of the irradiated gas provides evidence for CF_2 and CF_2Br as being major photolysis products. C_2F_4 was also found to cause etching at 248 and 193 nm. This is evidence that CF_2 , resulting from C_2F_4 photolysis, is alone capable of initiating glass etching in the presence of laser light. The paper concludes by discussing the observed inability of the CF_3 releasing parent gases CF_3Br and CF_3I to significantly etch glass when irradiated in their appropriate absorption bands.

Introduction

For some time, borosilicate glass has been considered as an electrical insulator for microelectronic applications.¹ Etching of thin glass films provides a means of generating surface relief relevant to dielectric applications. To date, only two reports on laser etching of glass have appeared. The first involved focusing a continuous wave CO_2 laser onto a glass surface in the presence of hydrogen fluoride.² The second technique utilized a 193-nm pulsed excimer laser together with hydrogen gas.³ Both methods relied on the laser to generate sufficient heat in the strongly absorbing glass to raise the surface to the softening temperature. Subsequent reaction with the gas led to a thermally induced etching. The purpose of this report is to demonstrate that glass etching can be initiated by a low-temperature, photochemical process.

For more than 30 years, gas-phase halogenated methanes have been known to undergo efficient photodissociation upon absorption of a light quantum.⁴ Only in recent years has this fact been utilized for microelectronic etching applications. In particular, photochemically generated halogen atoms,⁵ methyl radicals,⁶ trifluoromethyl radicals,^{6–8} and difluorocarbene radicals⁸ have been employed in laser-etching schemes for a variety of materials. The unreactive nature of the radical precursors constrains significant etching to occur in or near the laser light defined surface region. Brominated and iodated methanes are particularly amenable to excimer laser photolysis since their absorption bands are shifted to longer wavelengths relative to their fluoro and chloro analogues which typically absorb in the vacuum ultraviolet.⁴

It is against this background that laser-induced glass etching was attempted using CF_2Br_2 as the processing gas. The success of both this gas and C_2F_4 , using either 248- or 193-nm laser excitation, is striking since neither Br_2 , CF_3Br , CF_3I , SF_6 , nor air were observed to initiate significant etching.

Etching Experiments

Etching experiments were performed by irradiating glass samples contained in a closed, stainless steel cell of approximately 1.6 L total volume. Excimer radiation was provided by a Lambda

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	TAB	LE	I:	Etching	Result	s
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 gas	wavelength, nm	press., torr	etch rate, ^a Å/pulse
CF ₂ Br ₂	193	20	0.45
	248	20	0.50
	351	20	< 0.01
C_2F_4	193	100	0.60
	248	100	0.55
CF ₃ Br	193	500	< 0.01
-	193	300	<0.01
	248	20	< 0.01
CF₃I	248	80	<0.01
-	248	42	< 0.01
$Br_2 + Br$	248	2	0.03
SF_6	248	50	< 0.01
air	193	760	<0.01
vacuum	248	<10 ⁻⁴	< 0.01

^a The etch rates were performed at a gas incident fluence of 1 J/cm^2 .

Physik Model EMG 101 laser at several wavelengths. Pulse lengths were ~ 15 ns. By use of appropriate optics, the pulsed beam was incident on the glass surface in the form of a 1 mm \times 1 mm square. After the evacuated cell was cleaned and baked, a known pressure of a sample gas was admitted. An internal fan was used to draw the gas past the glass surface and circulate it to the back of the cell. The distance from the inside surface of the cell window to the glass surface was 1.5 cm.

Typical irradiation conditions were 15 min of exposure at a laser repetition of 10 Hz. Determination of the single pulse energy was made by measuring the average power of the laser at the 10-Hz operation rate on a ScienTech Model 38-0403 volume absorbing calorimeter. This was converted to average single-pulse fluence (in mJ/cm²) by use of the pulse energy and irradiation area, 0.01 cm². Glass surface incident fluences were not directly determined but rather estimated from the Beer-Lambert relation. Values of the pulse fluence were changed by use of nonbleachable attenuation filters. Etch depth measurements were performed on a stylus profilometer. All etched samples were cleaned of residue surrounding the etched region prior to the etch depth measurement. The average etch rate (in Å/pulse) was determined by dividing the total average etch depth by the total number of incident pulses.

Experiments were performed on 3-mm-thick pieces of Corning 7070 glass. This glass consists chemically of approximately 70% SiO_2 , 25% B_2O_3 , with the remainder being oxides of Al, K, Na, and Li.⁹ The gases CF_2Br_2 , CF_3Br , CF_3I , and C_2F_4 were obtained from PCR Chemicals. SF_6 was obtained from Matheson, while the bromine was supplied by Mallinckrodt. All gases were used as obtained without further purification. Experiments were

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KRF LASER ETCHING OF CORNING 7070 GLASS



Figure 1. Stylus trace across laser-etched area in glass.

performed at ambient room temperature.

The experimentally determined glass etch rates for several different processing gases and wavelengths are presented in Table I. All results in Table I were obtained at a fluence of 1 J/cm^2 , measured prior to transmission through the gas. The etch rate measurements are precise to 15%. Gas pressures ranged from 5 to 500 torr for the halogenated methanes and SF_6 , while air was examined at 1 atm. Etching attempts under vacuum were at a pressure of approximately 5×10^{-5} torr. Etching under vacuum, as well as in several of the other gases, produced only a rough morphological change on the surface similar to that shown in Figure 2c. Table I demonstrates that etch rates significantly larger than that for vacuum irradiation occur only with CF_2Br_2 and C_2F_4 . Additionally, significant etching with CF₂Br₂ was observed only at 193 and 248 nm and not at 351 nm. For the approximately 0.5 Å/(cm²/pulse) etch rate observed for CF_2Br_2 , a mass removal rate of 1.1×10^{-8} g/(cm²/pulse) can be calculated from the glass density value of ~ 2.3 g/cm³.

Figure 1 displays a typical stylus trace of an etched region on the glass surface. Figure 2 displays SEM photos of the surface areas depicted in profile in Figure 1. The transition region in Figure 2a between the nonirradiated region (upper left corner) and the etched region (lower right corner) is the same region as the left-hand "step" in Figure 1. The nonirradiated areas of Figure 2, a and b, are clearly much smoother than the irradiated area of Figure 2c which is rough. The chemical action of the gas on the surface apparently does not cause the roughness, since vacuum irradiation results in a similar rough surface.

When 2 torr of bromine was used as the processing gas, continuous light from a xenon arc lamp simultaneously irradiated the glass surface along with the laser pulses. The arc lamp radiation was spectrally filtered so that only light in the bromine photolysis band between 400 and 600 nm was incident on the sample. This method permitted bromine atoms to be continuously generated near the glass surface in the presence of intense UV laser pulses. By mildly focusing the lamp output with a lens, the total lamp flux incident on the glass surface was determined to be approximately 0.5 W/cm². The bromine etch rate of ~0.03 Å/pulse is significantly less than the CF₂Br₂ etch rate.

Experimental results of the etch rate dependence on surface fluence for three different CF₂Br₂ pressures are presented in Figure 3. The reported surface fluences are estimated from the measured fluences incident on the gas and the Beer-Lambert law. The estimated values should be approximately correct as long as significant CF₂Br₂ decomposition does not occur (see Figure 4). Experiments have indicated that with the etching conditions used, i.e. internal circulation of the gas coupled with a large cell volume (1600 cm³), the gas transmission does not significantly change during the etching period. The etch rate data of Figure 3 assume a 1-cm² incident area. The etch rate is observed to regularly increase with increasing surface fluence at constant pressure. Similarly, for a constant fluence, higher gas pressures produce larger etch rates. The initial slope of the curves decreases on going from a pressure of 20 to 5 torr. Significant surface etching will begin at approximately 300 mJ/cm² for the 20-torr case, while it is a factor of 2 higher at 5 torr. It is worth noting that significant



Figure 2. Scanning electron microscope (SEM) photos of laser-etched and nonetched areas on glass surface. (a, top) Transition region between nonirradiated area (upper left region) and laser etched area (lower right region). Magnification, 800×. (b, middle) High magnification (8000×) of nonirradiated region in photo (a) showing smooth surface. The object in the photo was for SEM focusing purposes only. (c, bottom) 10000× magnification of laser-etched region in photo (a) displaying a rough surface.

etching was not observed from vacuum irradiation at fluences up to 2.5 J/cm^2 . Vacuum ablation clearly occurred for fluences between $3.5 \text{ and } 4 \text{ J/cm}^2$.

GLASS ETCH RATE VS & AND P



Figure 3. Plot of glass etch rate vs. estimated surface fluence for three different CF_2Br_2 pressures.



Figure 4. Plot of high (laser) intensity gas transmittance vs. time for a static, nonflowing, gas sample. The laser repetition rate was 10 Hz. 10 min corresponds to 6000 pulses.

Absorption Properties of CF₂Br₂ and Glass

Walton¹⁰ has determined that under low light intensity conditions (as in a conventional spectrophotometer) gaseous CF_2Br_2 absorbs light with an absorption cross section of 1.1×10^{-18} cm² at 248 nm and 2.4×10^{-18} cm² at 193 nm. Near 300 nm the cross section has fallen to approximately 10^{-21} cm², and at 351 nm the absorption is negligible. These values can be compared to the absorption properties of gaseous CF_3Br and CF_3I which were also examined as glass etchants. CF_3Br does not appreciably absorb at 248 nm¹¹ but does at 193 nm with a cross section of 8×10^{-20} cm²—a factor of 30 less than CF_2Br_2 at the same wavelength. CF_3I will not significantly absorb at 193 nm, but at 248 nm possesses a 2.6×10^{-19} cm² absorption cross section.¹² This value for CF_3I is a factor of 4 less than that of CF_2Br_2 at 248 nm.

As one means of investigating the photochemical properties of CF_2Br_2 , the transmission of 248-nm laser pulses through the gas

was measured as a function of the number of pulses. With the laser operating at 10 Hz, and at an incident fluence of 1 J/cm^2 , transmission readings were collected every 30 s for a period of 10 min. During this experiment, the 1 cm path length gas transmission cell was filled with 10 torr of CF₂Br₂ in a total cell volume of 5 cm³. A plot of the experimental data is shown in Figure 4. The high-intensity transmission is seen to rise from an initial value of 0.75 to 0.93 after 6000 laser pulses. The same gas cell was used to monitor the transmission of 10 torr of CF_2Br_2 at 248 nm in a conventional UV spectrophotometer for 10 min. When corrected for cell window losses, this low-level transmission was found equal to 0.775. The change in the low-level transmission was only 0.001 units over the 10-min period. When a literature value¹⁰ for the 248-nm absorption cross section of very pure CF₂Br₂ at a precisely known concentration is used, a transmission of 0.69 is calculated for a 1-cm path length. Evidently, the high-intensity transmission is initially equal to the low-level value until "bleaching" occurs. The bleaching results from the photodecomposition of CF₂Br₂. CF₂Br₂ photochemistry will be discussed

Determination of the glass absorption coefficient requires a knowledge of the glass reflectivity. Therefore, high-intensity reflection measurements were made and compared to the low-level values. A quartz beam splitter, placed in the path of the incident laser beam, directed a small fraction of the light toward an energy meter calibrated so as to measure the pulse energy incident on the glass sample. A second energy meter was placed in front of the glass sample but $\sim 15^{\circ}$ off the surface perpendicular. Intense laser pulses, about 1 J/cm², incident on the smooth glass surface were specularly reflected back onto the second energy detector. The ratio of the reflected energy to the incident energy gave the experimental value of the reflectivity. At 248 nm the measured reflectivity is 0.042, while at 193 nm the value is 0.053. The 3-mm thickness of the glass sample absorbed enough radiation to assure that reflection from only one surface was being measured. Low-intensity values of the reflectivity can be calculated from the Fresnel equations.¹³ For a glass refractive index varying between 1.5 and 1.6 (as it would between 250 and 190 nm), the near normal reflectivity is found to range from 0.04 to 0.05 as is well-known. The high-intensity surface reflection is thus found to equal that at low levels.

in the next section.

The low-level glass absorption coefficient at 248 and 193 nm was estimated from the measured transmission spectrum of thin glass samples and the reflectivity values. A thick piece of Corning 7070 glass was heated to the softening point with a gas torch and blown into a very large sphere. When the sphere had cooled, a small section measuring 60 μ m in thickness was broken off and removed. The sphere had been large enough so that any curvature of the thin sample was negligible. The UV transmission through this piece was measured on an IBM Instruments Model 9430 UV-visible spectrophotometer. This spectrum is displayed in Figure 5. The total transmission through a thick piece of glass can be calculated by the following:

$$T = \left[t(1-r)^2 \right] / \left[1 - (tr)^2 \right]$$
(1)

In eq 1 T is the total transmission, r is the single surface reflectivity, and t is the internal transmittance of the glass. t is usually assumed to follow the Beer-Lambert law, $t = \exp[-\alpha x]$, where α is the absorption coefficient and x is the material thickness. Equation 1 assumes that the sample thickness is greater than the coherence length of the spectrophotometer light source, a condition that easily holds for these measurements. Knowing r and T at the two excimer laser wavelengths allows the values of t to be calculated from eq 1. In turn, α can be estimated from the knowledge of t and the sample thickness. Absorption coefficients obtained in this manner are listed in Figure 5.

A value for the high-intensity absorption coefficient of the glass was estimated by using a transmission measurement technique similar to that used to obtain Figure 4. 248-nm laser radiation

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Laser Etching of Glass with CF₂Br₂

TRANSMISSION SPECTRUM OF 7070 GLASS (60 µm thick)



Figure 5. Low-intensity transmission spectrum of Corning 7070 glass. The absorption coefficients for two excimer laser wavelengths appear in the upper left corner of the spectrum. See text for discussion as to how the values were derived.

FLUORESCENSE OF 248 NM EXCIMER LASER IRRADIATED CF2BR2



EMISSION DUE TO
$$CF_2$$
: $\widetilde{A} \, {}^1B_1 \longrightarrow \widetilde{X} \, {}^1A_1$

Figure 6. Fluorescence emission spectrum of 248-nm irradiated CF₂Br₂. The emission, assigned to CF₂, was analyzed by using 10-Hz laser fluences of 0.5 J/cm^2 and 1 torr of gas.

at 10 Hz and 1 J/cm² was used for the transmission measurement. The measurements were repeated seven times to give an average transmission $T = I/I_0 = 0.31$. The high-intensity absorption coefficient calculated from eq 1 is then $\alpha = 45.3 \text{ cm}^{-1}$. The similarity of this figure to the low-level value, given in Figure 5, indicates that, even under laser-etching conditions, the glass surface is not strongly absorbing.

CF₂Br₂ Photophysics and Photochemistry

During glass etching at 248 nm with CF_2Br_2 , a bright blue-violet emission is observed from the gas. Although etching also occurs with 193-nm radiation, visible emission is not observed in this case. Spectroscopic analysis of the luminescence excited at 248 nm revealed the difluorocarbene radical, CF₂, as the emitting species. A Spex 1/2-m monochromator coupled to a PAR/EGG Model 162 boxcar averager produced the CF₂ spectrum displayed in Figure 6. CF₂ emission spectra from excimer laser irradiated CF_2Br_2 have been observed previously by others^{14,15} and assigned to the $A^1B_1 - X^1A_1$ transition.



Figure 7. Low-level absorbance of 248-nm laser irradiated and nonirradiated gaseous CF₂Br₂ vs. wavelength: (A) nonirradiated gas; (B) after 10 min of laser irradiation at 10 Hz; (C) absorbance due to evacuated cell.

To investigate the gas-phase photochemistry of CF₂Br₂ under intense pulsed laser conditions at 248 nm, approximately 3 torr of the gas in a conventional 10-cm-long absorption cell was irradiated under conditions similar to that used for glass etching. UV, visible, and IR absorption analysis of the irradiated gas demonstrated the following gases to be present: CF_2Br_2 , $(CF_2Br)_2$, small amounts of Br₂, and possibly gaseous C₂F₄. The UV and visible work was performed by placing the irradiated cell directly into an IBM Instruments 9430 spectrophotometer and measuring the gas absorption spectrum. Figure 7 displays the UV absorption spectrum of CF₂Br₂ gas both before and after laser irradiation. In keeping with the data of Figure 4, the initial absorption is observed to permanently "bleach" and cause the appearance of a new spectrum with a weak, broad shoulder centered near 208 nm. This shoulder is likely due to $(CF_2Br)_2$ which should have approximately the same spectral maximum as do CF₃Br and C₂F₅Br.¹¹ The background continuum rising into the vacuum UV may be due to C_2F_4 .¹⁶ A weak visible spectrum occurring between 350 and 500 nm was identified as due to Br₂.⁴ For the IR work, a second evacuated absorption cell with KBr windows was attached to the UV photolysis cell via a vacuum valve. After the laser irradiation period, the valve between the two cells was opened allowing gases to flow into the IR cell. After detachment of the cells, the IR cell was placed in a Perkin-Elmer Model 580 IR spectrophotometer for absorption analysis. The IR spectra of CF_2Br_2 before and after laser photolysis are shown in Figure 8. Careful examination of the lower part of Figure 8 and comparison with literature spectra show $(CF_2Br)_2^{17}$ and residual CF_2Br_2 to be present. The presence of C_2F_4 cannot be precisely identified in Figure 8 due to the overlap of its spectrum with that of the other gases.18

Another example of the photochemical properties of CF₂Br₂ is the occurrence during laser irradiation at either 193 or 248 nm of a polymer deposit around the etched area on the glass surface and on the etching cell window near where the pulses enter the cell. IR absorption analysis of this solid material demonstrates it to be very similar to Teflon, as shown in Figure 9. Teflon, a

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Figure 8. Infrared spectra of gaseous CF2Br2 before and after 248-nm laser irradiation: top, spectrum of nonirradiated CF₂Br₂; bottom, IR spectrum after laser irradiation. The peaks labeled "a" are due to generated (CF₂Br)₂.



Figure 9. IR spectrum of the photogenerated polymer (bottom trace) compared to that of pure Teflon (upper trace).

poly(tetrafluoroethylene) polymer, is composed of CF₂ monomer units.

The identification of $(CF_2Br)_2$ from the above photochemical studies suggests that CF₂Br radicals are precursors to (CF₂Br)₂ formation. Likewise, CF₂ radicals have been confirmed by emission analysis (Figure 6), and from IR analysis of the polymer (Figure 9). These results dictate that both CF_2 and CF_2Br radicals are present during the high-intensity laser photolysis of CF₂Br₂. This is consistent with previous observations using nonlaser, low-intensity photolysis methods.^{10,19,20}

The photochemical aspect of CF_2Br_2 that still remains unclear, after nearly 30 years of research, is the mechanism of CF₂ production. In 1961, Simons and Yarwood²¹ reported that UV flash photolysis of CF₂Br₂ produced CF₂ and concluded that CF₂Br radicals are not the precursors to CF₂ formation. They considered the molecular elimination mode as the means for CF_2 production:

$$CF_2Br_2 + h\nu \rightarrow CF_2 + Br_2$$
 (2)

However, other groups have claimed that bromine elimination is the primary mode of CF₂Br₂ photodecomposition:^{10,19,20,23,24}

$$CF_2Br_2 + h\nu \rightarrow CF_2Br + Br$$
 (3)

The first excimer laser experiments on the photolysis of CF₂Br₂ were reported in 1979 by Sam and Yardley who concluded eq 2 to be the mode of CF_2 production.¹⁴ That same year Wampler et al.¹⁵ also reported on the 248-nm excimer laser photolysis of CF_2Br_2 with a similar conclusion that eq 2 was correct. More recently, Krajnovich et al.25 studied the low-pressure photochemistry of CF₂Br₂ at 248 nm by a crossed excimer laser-molecular beam technique. They concluded that the primary reaction channel in CF_2Br_2 photodissociation is eq 3, in agreement with the much earlier work of Tedder and Walton²³ and Walton.¹⁰ Krajnovich et al. account for CF_2 production by CF_2Br absorbing a second photon and eliminating Br. They deduce that CF₂Br possesses an absorption cross section at 248 nm of at least ten times that of CF_2Br_2 , although the exact value for CF_2Br depends on its internal energy.

Discussion

There exist two reasons why the initiation of glass etching is considered principally nonthermal. The first is the low value of the glass absorption coefficient, as displayed in Figure 5. For 248-nm radiation, either a simple energy balance equation²⁶ or a one-dimensional heat flow calculation²⁷ demonstrates that the temperature rise of the glass over the laser light absorption depth is <10 °C per pulse for the conditions used in these studies. Secondly, Table I shows that significant glass etching does not occur at 351 nm, a region where CF_2Br_2 does not absorb. Although the glass absorption coefficient is decreasing over the wavelength range 248 to 351 nm (40 to 5 cm⁻¹), going from a negligibly small value to an even smaller one does not change the argument. Absorption of laser photons by CF₂Br₂ gas appears to be a necessary condition for etching to occur. If, however, CF_2Br_2 were capable of chemisorbing onto the glass surface to a significant degree, this would provide a means by which laser energy could be coupled into the glass and heat the surface. However, it is unlikely that CF_2Br_2 will chemisorb, since similar halogenated methanes have not been observed to chemisorb.28

From the 248-nm laser photolysis studies of CF₂Br₂ reported above, it cannot be clearly determined whether the principle photolysis intermediate is CF_2 or CF_2Br . The observed photoproduct, $(CF_2Br)_2$, could be formed in three ways. The first is through reaction of two CF₂Br radicals. Secondly, if two CF₂ species combine to give C_2F_4 , then addition of Br_2 across C_2F_4 would yield the same product. Thirdly, CF₂ could insert between the C-Br bond in CF_2Br_2 . Although nothing is reported in the literature on this third mechanism, it is considered unlikely in analogy to the concluded unreactivity of CF₂ toward CF₂Cl₂.²⁹ In a paper on the photochemistry of CF₂ClBr, Taylor et al.³⁰ conjectured that both CF₂Cl and CF₂ are initial photolysis products that form with differing quantum yields ($CF_2Cl > CF_2$) at the wavelength studied. By analogy to the work of Taylor et al. and the results of this study and several others mentioned previously, it is accurate to assume that both CF_2 and CF_2Br are formed during the photolysis of CF_2Br_2 .

Having considered the photochemistry of CF₂Br₂, one finds that a principal question becomes: which photofragment is responsible for initiation of the glass etching? For several reasons, CF_2 is likely to be that species. Molecular or atomic bromine apparently

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makes no significant contribution to glass etching by itself. This is shown in Table I. At the 2-torr pressure of bromine used in the etching experiment, a rough calculation indicates that the concentration of bromine atoms (generated by the arc lamp) within several mean free paths of the glass surface far exceeds the same concentration of bromine atoms generated near the surface by the photolysis of CF_2Br_2 (10 torr total pressure). The other photoproduced radical, CF₂Br, cannot be a priori ruled out as a glass etchant. Once formed, CF₂Br will undergo a random walk process colliding with its most probable collision partner, CF₂Br₂. Any reaction that occurs between CF_2Br and CF_2Br_2 will likely result in bromine abstraction from CF_2Br_2 and creation of a new CF₂Br species. This propagation reaction might continue until a given CF₂Br species contacted the glass surface. However, if CF_2Br is similar in reactivity to CF_3 , then the probability of a given CF₂Br moiety diffusing to the glass surface without reacting with another CF_2Br species is greatly lessened relative to CF_2 . For the room temperature reaction $2CF_3 \rightarrow C_2F_6$ the second-order rate constant is $3.4 \times 10^{11} \text{ L/(mol s)}$, whereas for $2\text{CF}_2 \rightarrow \text{C}_2\text{F}_4$ the rate constant is $1.7 \times 10^7 L/(mol s)$ ²² In this regard singlet CF_2 is a surprisingly stable species. As will be discussed below, CF₃ releasing gases were not observed to cause significant glass etching. By analogy, CF₂Br may be an inefficient etchant. Additionally, based on the work of Krajnovich et al.,²⁵ there seems to be a large propensity for CF₂Br to undergo photolysis and form CF₂ and Br. Such a process would further reduce the near surface concentration of CF₂Br and tend to increase the CF₂ concentration.

To shed further light on the question of CF_2 and CF_2Br , etching experiments were conducted which used C_2F_4 as the processing gas. C_2F_4 absorbs low-intensity 193-nm light with a cross section of 10^{-19} cm², but it exhibits negligible absorption at 248 nm.¹⁶ With 248-nm KrF laser pulses in 100 torr of C_2F_4 , etching occurred at a rate of approximately 0.6 Å/pulse. During etching at 248 nm, we observed a blue-violet gas emission. When the laser wavelength was changed to 193 nm, etching occurred at the same rate, but no gas-phase emission was detected. At both wavelengths, a surface polymer formed. This is identical with the observations on CF_2Br_2 photolysis, and the emission observed from C_2F_4 photolysis at 248 nm is ascribed to CF_2 . Apparently, C_2F_4 photolysis at 248 nm results from two-photon absorption. According to eq 4, CF_2 should cleanly result from C_2F_4 photolysis with no unwanted chemical products:

$$C_2 F_4 \rightarrow 2 C F_2 \tag{4}$$

The fact that glass etching occurs with C_2F_4 provides strong evidence that CF_2 is capable of etching glass in the presence of excimer laser irradiation.

In light of the preceding discussion, the results of Figure 3 can be partially explained on the basis of gas-phase radical concentration. At any of the pressures in Figure 3, increasing the surface fluence will cause a corresponding increase in the near surface radical concentration as dictated by the photolytic properties of CF₂Br₂ and the Beer-Lambert law. Insofar as the radical concentration is proportional to the rate of surface etching reactions, it follows that the etch rate should increase with increasing radical concentration. Similarly, at a given fluence, increasing the pressure from 5 to 20 torr will cause an increased etch rate. Qualitatively, the observed increase in initial slope with increasing pressure is expected. The number of absorbed photons per unit volume, A (proportional to the nascent radical concentration), can be easily determined from the Beer-Lambert law: $A = I_0(1 - T)$, where I_0 is the number of photons incident on a given unit area, and T is the gas transmission through a unit distance near to the surface. Differentiating yields $dA/dI_0 = 1 - T$. Thus as the pressure increases (decreasing T), dA/dI_0 increases. Since dA/dI_0 should be proportional to the slope in Figure 3, the result is understood. Missing from the above argument is the role of surface photochemical processes, which may affect the relation between etch rate and fluence. Such questions are beyond the scope of this report.

Table I shows that irradiated CF₃Br and CF₃I do not cause any significant etching of glass when irradiated in the appropriate absorption band. Etching experiments were conducted in which the estimated optical densities of CF₃Br and CF₃I were less than, equal to, and greater than that used for CF_2Br_2 under conditions when glass etching is achieved. This permitted the same number of photons to be absorbed per unit volume for each gas. The photodissociation quantum yields for all three species are within a factor of two (56% for CF_3Br ,¹¹ 75% for CF_3I ,¹² and 100% for $CF_2Br_2^{20}$). It can then be assumed that CF_3 concentrations initially formed from CF₃Br or CF₃I are of the same magnitude as the total concentration of CF_2 and CF_2Br initially formed from CF_2Br_2 . Due to the smaller absorption cross sections of CF_3Br and CF₃I, larger gas pressures are required to make their optical densities similar to the stronger absorbing CF_2Br_2 . As a result, CF₃ will undergo many more gas-phase collisions on its diffusion toward the glass surface than will CF_2 from photolyzed CF_2Br_2 . For example, CF_3Br at 300-torr total pressure has a mean free path of approximately 0.2 μ m, while that of CF₂Br₂ at 10 torr is 4 μ m. This will increase the probability of CF₃ reacting with another species before the glass surface is contacted. Increasing the optical density (pressure) of CF₃Br or CF₃I to generate more CF₃ will only exacerbate the problem. A resulting low near-surface concentration of CF3 may explain why etching is not observed for CF_3 releasing parent gases. Alternately, CF_3 may be an inherently inefficient glass etchant. This point seems to be corroborated in a study by Loper and Tabat⁸ who observed poor etching of silicon dioxide when CF₃ releasing precursor gases were employed. In contrast, these authors observed CF₂ producing gases to clearly etch silicon dioxide. Harridine et al. observed etching of SiO₂ (~ 0.3 Å/pulse) by using pulsed CO₂ laser dissociation of CF₃Br.⁷ Their claim was that photoproduced CF₃ was the etchant. For their experiments, the laser was incident parallel to the surface and focussed approximately 1 mm above the surface. Their result stands in contrast to the work of this paper and that of Loper and Tabat. If the experiments of Harridine et al. produced highly vibrationally excited CF₃, then the difference between the CO_2 and excimer laser work could possibly be rationalized. However, Harridine et al. make no statement concerning this possibility.

Summary

This report has provided evidence that, in the presence of an intense photon field, CF₂ radicals from photolyzed CF₂Br₂ are capable of etching SiO₂-based materials. An interesting question is to what degree vibrational and/or electronic excitation of CF_2 influences the etching efficiency. A partial answer lies in the etching results from both 193- and 248-nm irradiation. With 248-nm etching the ${}^{1}B_{1}$ state of CF₂ is readily populated, enabling electronic excitation of CF₂ species in contact with the glass surface. This situation does not occur when using 193-nm radiation due to the small absorption probability of CF_2 at this wavelength.³¹ However, the observed etch rates for both wavelengths are similar, suggesting that electronic excitation of CF_2 does not significantly influence the etch rate. More sensitive surface techniques would be required in order to quantify the difference between ${}^{1}A_{1} CF_{2}$ and ${}^{1}B_{1} CF_{2}$.

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Registry No. CF_2Br_2 , 75-61-6; CF_2 , 2154-59-8; CF_2Br , 28882-09-9; C_2F_4 , 116-14-3; CF_3Br , 75-63-8; CF_3I , 2314-97-8; SF_6 , 2551-62-4; Br_2 , 7726-95-6; Br, 10097-32-2.

⁽³¹⁾ C. W. Mathews, Can. J. Phys., 45, 2355 (1967).