Halofluorocarbon plasma treatments of polystyrene and poly(methyl methacrylate) surfaces

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The effect of halofluorocarbon (CF_4, CF_3Cl, CF_3Br) discharges on polystyrene (PS) and poly(methyl methacrylate) (PMMA) has been studied. It has been shown that, depending on the halogen/halocarbon radical ratio, polymerization or etching can occur. The discharge chemistry has been altered by changing the excitation electrode material, and thus enhancing or depressing the amount of halocarbon radicals in the discharge. In CF_3Br and CF_3Cl plasmas, mass spectroscopy revealed the formation of molecular chlorine and bromine. Ion bombardment has been shown, in both PS and PMMA, to enhance etch rates and to depress the deposition of plasma polymer. While the etch rates of PMMA by CF_4, CF_3Cl and CF_3Br have the same kinetic dependence on bias voltage, the same is not true for PS. In this case the etch rates by CF_3Cl and CF_3Br discharges are preferentially enhanced, due to the different interaction with the species present in the discharge. As to derivatization, the introduction of halogens is more efficient in PS than in PMMA. Interestingly, the introduction of Cl and Br is enhanced much more than that of F, possibly due to the interaction of the PS aromatic ring with molecular chlorine and bromine present in the discharge.

(Keywords: plasma; halofluorocarbon; surfaces; polystyrene; poly(methyl methacrylate))

INTRODUCTION

The treatment of polymeric surfaces using a low pressure non-equilibrium plasmas has long been established[1–4]. Discharges in halogen-containing gases have frequently been used on polymers. The aims of the studies varied, including plasma etching of photoresists[5,6] and surface derivatization, and most frequently, fluorination[7,8].

In this work we studied the effect of halofluorocarbon discharges on polystyrene (PS) and poly(methyl methacrylate) (PMMA). PS is a vinyl-type polymer (relatively insensitive positive resist)[9]. Noble gas and oxygen plasma treatments have been reported[10,11]. In contrast, PMMA is a vinylidene-type polymer (very efficient negative resist)[9]. The effects of noble gas, oxygen and CF_4/O_2 mixture plasmas have been reported[4,12,13].

Halofluorocarbon gases are used very frequently in dry etching processes in the electronic industry, since their halogen rich plasmas are quite effective in promoting etching[14,15]. Their use in altering the surface chemistry of polyethylene[16] and polypropylene[17] has been reported. Yagi *et al.*[16] did not distinguish between fluorination due to polymerization or derivatization, while Strobel *et al.*[17] showed that the formation of plasma polymers from CF_4, CF_3Cl and CF_3Br did not occur. Neither tried to relate the effect of the treatment on the surface to the discharge chemistry.

When treating polymer surfaces with halofluorocarbon plasmas many reactions are possible, both in the discharge and at the substrate/plasma interface. The possible consequences are: deposition of a plasma polymer layer on top of the substrate, ablation (etching) of a surface layer, and change of composition at the surface (derivatization). It is possible to find out whether deposition or etching occurs using gravimetric methods, in our case quartz crystal microbalances (QCM). We tried to relate etching and deposition rates to the discharge chemistry and to parameters such as the sample bias voltage. The change of surface composition is obvious in polymer deposition and we will not discuss that. Instead we address the problem of how the surface composition changes during etching and how it depends on the discharge chemistry.

EXPERIMENTAL

Commercial PS (Edistir 20100) and PMMA (Vedril) were used. No attempt was made to extract the additives normally present in the polymers. The samples for plasma treatment were prepared as follows: 5% (w/v) solutions of the polymer in chloroform were spin coated on gold-coated quartz crystals, to yield uniform films with average thickness about 10 μm. The samples were then heated under vacuum to remove the solvent completely. The surface of the sample exposed to the plasma was circular, with a 0.5 cm diameter. CF_4 (Freon 14), CF_3Cl (Freon 13) and CF_3Br (Freon 13B1) were purchased from Matheson in the form of lecture bottles.

The experimental arrangement for plasma treatments used in this work has been described previously[18]. It consists of a 15 cm diameter excitation electrode to which 13.56 MHz radio frequency (r.f.) power is applied through a blocking capacitor. Silicon dioxide and carbon

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excitation electrodes were used to study their effect on the discharge chemistry. The gas flow was always kept at 6 cm^3 (s.t.p.) min^{-1} and the system pressure was normally held at 10 mTorr (1.333 Pa). Owing to the small polymer surface exposed to the plasma (about 0.8 cm^2) and to the volume of the plasma chamber (about 90 dm^3), the etching of polymers does not alter the chemistry of the discharge.

Etch rates have been measured using two QCMs inserted into the glow discharge between the electrodes, with the surface located at 10.2 cm from the centre of the discharge. The bias voltage was applied to one of the QCM holders using a capacitatively coupled 13.56 MHz r.f. generator. The second QCM holder was held at ground potential and the etch rates were monitored while the other QCM was biased, to make sure that the bias did not affect the overall glow discharge.

Our experimental arrangement allowed recording of the u.v.-visible emission spectrum of the discharge. A Hilger and Watts single grating D330 monochromator, interfaced with an electrometer and a 7090A HP plotting system, was used for this purpose. The addition of 3% Ar to the gas feed allowed us to perform actinometry. The triplet atomic line of Ar (750.4 nm) was used as a reference. For fluorine the 703.7 nm atomic line was chosen, while halocarbon radicals are responsible for a broad continuum located between 200 and 350 nm.

The apparatus was also interfaced with a mass spectrometer (SpectraScan 759 system, built by Granville–Phillips). Both neutral molecules and ions coming from the discharge could be analysed. The optics necessary for the extraction of positive ions from the discharge has been extensively described elsewhere[19].

X-ray photoelectron spectrometry (X.p.s.) spectra were measured *ex situ* on a PHI model 548 X.p.s.-AES spectrometer, using the Mg Kα radiation (1253.6 eV) from a 400 W source. The analysis chamber pressure was maintained near 2×10^{-7} Pa, without baking. Signal averaging to improve the signal-to-noise ratio was possible due to the connection of the spectrometer to a PDP 11/50 computer. Further data processing (smoothing, background subtraction, integration, deconvolution) was carried out using in-house software on a Sperry 1100/72 mainframe computer. The hydrocarbon C-1s peak was used as a reference and set to 284.6 eV. Surface compositions were calculated from the spectra using the appropriate sensitivity factors[20].

RESULTS

Discharge chemistry

The balance between etching and polymerization can be shifted by altering the relative amount of halogen atoms and halocarbon radicals in the discharge[21]. One of the ways to do this is to use different excitation electrodes. The rate of reactions occurring at the excitation electrode is very high, since there is acceleration by ion bombardment[14]. It is therefore possible to tune the gas chemistry by changing the electrode material. We used electrodes made of pyrolitic carbon and silicon dioxide. In the latter case, reactions leading to the formation of SiF_4 and carbon monoxide occur. As a result of these reactions the halogen/halocarbon radical ratio is increased, and thus etching and derivatization are favoured. In contrast, the use of a pyrolitic carbon electrode induces enhancement of the halocarbon radicals, due to the reaction of the target with halogens, leading to deposition of plasma polymers[14].

To understand the discharge chemistry we studied the optical emission spectra first. Coburn *et al.*[22] and d'Agostino *et al.*[23] demonstrated the possibility of measuring relative particle densities of a plasma by combining its emission intensities with the excitation efficiency of an excited level of a noble gas, added in small amounts.

In the 650–800 nm region, emissions from F, Cl, Br and Ar atoms are present, while in the 200–350 nm region broad bands due to halocarbon radicals are located[22,23]. In *Figure 1* the actinometric intensity ratios are reported for the two different excitation electrodes. In particular, *Figure 1(a)* shows that for the SiO_2 electrode the F/Ar ratio (proportional to the quantity of atomic fluorine in the discharge) decreases in the order $CF_4 > CF_3Cl >$

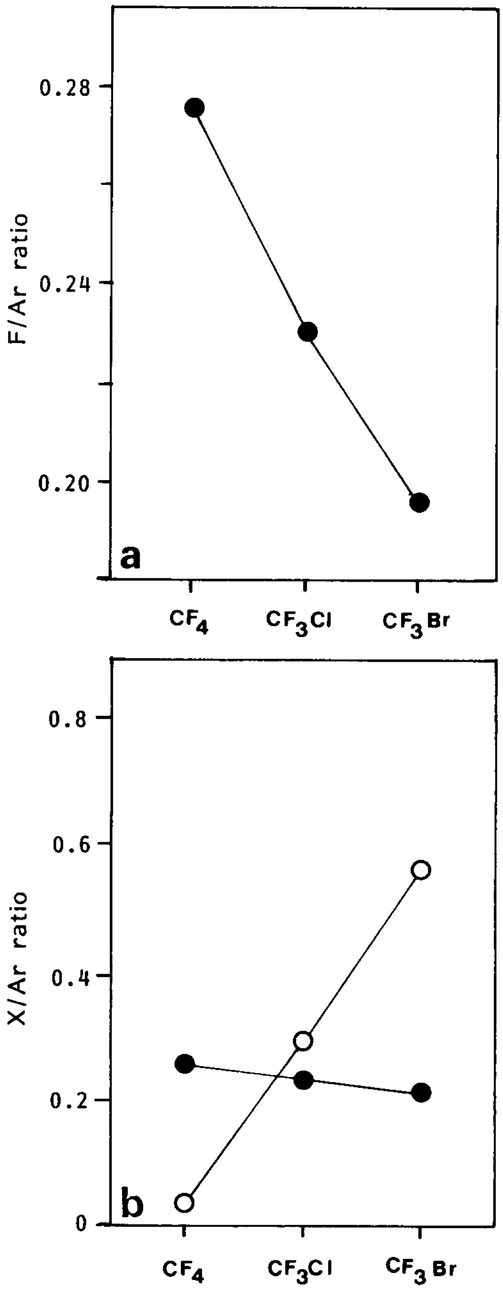

Figure 1 (a) Actinometric F/Ar ratios for halofluorocarbon discharges (SiO_2 excitation electrode). (b) Actinometric F/Ar (●) and CX_y/Ar (○) ratios for halofluorocarbon discharges (carbon excitation electrode)

CF_3Br; chlorine and bromine were, of course, detected as well. *Figure 1(b)* shows that, for the carbon electrode, fluorine has the same trend as for the SiO_2 electrode, while the number of halocarbon radicals in the discharge increases in the order $CF_4 < CF_3Cl < CF_3Br$. The same trend is valid for the SiO_2 electrode, but the intensity of the halocarbon continuum is much lower, due to the consumption by etching of the target.

A lot of work has been done on the mass spectrometry of glow discharges[24,25]. It has been shown that the extraction and characterization of ions present in glow discharges is particularly useful[24,25] for two reasons. The first reason is sensitivity: the ion spectra are far richer in observable species relative to the spectra of post-ionized neutrals. The second is that the ionization of neutrals induces fragmentation, thereby introducing uncertainty. For instance, the mass spectroscopy of ions has been shown to provide important insights into the plasma chemistry of fluorocarbon gases such as C_2F_4 and C_2F_6 (ref. 19).

For the silicon dioxide electrode we used mass spectrometry to gain further insights into the chemistry of CF_4, CF_3Cl and CF_3Br discharges. The mass spectra of both ions and neutrals coming from the discharge were collected – the spectrum of ions is more directly related to the discharge chemistry. The gas spectrum in the absence of the discharge was also recorded for comparison. For the carbon electrode extensive polymerization did not allow us to obtain meaningful results with mass spectroscopy.

In *Figure 2* the spectra of the ions from the CF_4, CF_3Cl and CF_3Br discharges are shown. The spectrum relative to the CF_4 discharge shows limited changes with respect to the spectrum of the plain gas (*Figure 2a*). It is dominated by the CF_3^+ fragment (69 Daltons). Other peaks relative to fluorocarbon fragments are present at 51 Daltons (CF_2H^+) and 31 Daltons (CF^+). The reaction with the target is represented for the silicon dioxide electrode by silicon and oxygen containing peaks, in particular COF^+, COF_2^+ and $SiOF^+$ (43, 66, and 63 Daltons, respectively). Weak peaks relative to fluorocarbon oligomers are present, for instance $C_2F_5^+$ and $C_3F_5^+$ fragments (119 and 131 Daltons).

In the spectra relative to CF_3Cl discharges silicon dioxide etching products and fluorinated oligomers are again present. More interestingly, in the ion spectrum intense peaks due to molecular chlorine ions (9:6:1 isotopomers at 70, 72 and 74 Daltons) are present (*Figure 2b*). Molecular chlorine has also been detected in the mass spectrum of neutral species. Peaks at 101, 103 and 105 Daltons are due to $CFCl_2^+$. In the mass spectrum of ions extracted from the CF_3Br discharge (*Figure 2c*), the formation of molecular bromine is evident due to the presence of the 1:2:1 triplet at 158, 160 and 162 Daltons. The triplet at 187, 189 and 191 Daltons is relative to $CFBr^{2+}$, formed in the discharge. A general observation is that in the CF_3Cl and CF_3Br discharges a lot of chemistry is going on, with the formation of species, such as halogen molecules, not present in the gas feed. The observation of ion spectra, thereby avoiding fragmentation due to ionization of neutral species, proves the point unambiguously.

The mass spectrum relative to the CF_3Cl plasma (*Figure 2b*) is more interesting. The peak at 85 Daltons, which dominates the spectrum, is due mostly to CF_2Cl^+, but partly to SiF_3^+, as shown by deviation of the isotopomer ratio from its ideal value (3:1). The other fragmentation pattern passes through C–Cl bond breaking and is shown by the presence of CF_3^+ peaks. The most intense fragment relative to an etching product is SiF_3^+ (85 Daltons), pointing to the well known fact that silicon dioxide is etched by fluorine but not by chlorine[14,15].

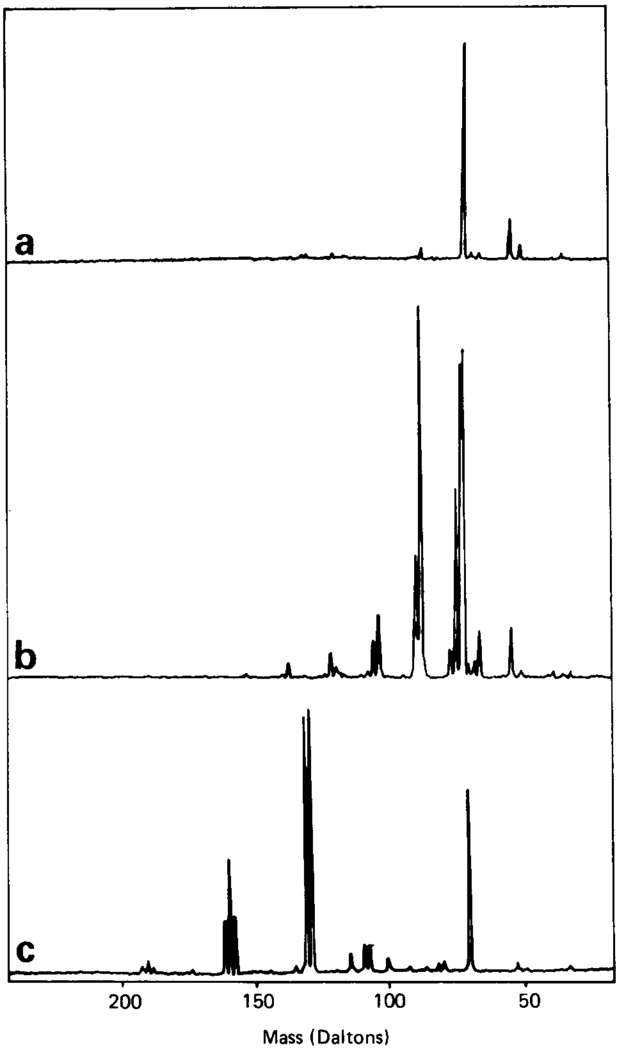

Figure 2 Mass spectrum of the ions extracted from the discharge (SiO_2 excitation electrode): (a) CF_4, (b) CF_3Cl, (c) CF_3Br

The presence for both electrodes of molecular chlorine (peaks at 70, 72 and 74 Daltons with intensities 9:6:1) in the discharge gives evidence of discharge-induced reactions. The drive to the formation of chlorine rich product is further evidenced by the presence of $CFCl^{2+}$ fragments (9:6:1 pattern at 101, 103 and 105 Daltons). Mixed chlorofluorocarbon oligomers are formed as well. The spectrum relative to CF_3Br plasmas is presented in *Figure 2(c)*. The trend is similar to that observed for CF_3Cl. The most important peaks are CF_2Br^+ (129 and 131 Daltons, intensities 1:1) and CF_3^+. The formation of molecular bromine is evident due to the 1:2:1 triplet at 156, 158 and 160 Daltons. $CFBr^{2+}$ is also formed (187, 189 and 191 Daltons).

The summary of these observations is that the consumption of fluorine in the etching of the target, silicon dioxide, enhances the discharge chemistry, leading to chlorine and bromine rich compounds. In CF_3Cl and CF_3Br plasmas the discharge is made deficient in fluorine and fluorocarbon species. Further reactions lead to the formation of chlorine and bromine rich ions and end up in the formation of molecular chlorine and bromine ions.

The spectra of neutrals (i.e. obtained using the ionization stage) confirmed the enrichment in chlorine and bromine containing species and the formation of molecular halogens.

Etching versus polymerization

Etching and deposition rates in CF_4, CF_3Cl and CF_3Br discharges for both silicon dioxide and pyrolitic carbon electrodes were obtained using QCMs. In *Figure 3a* the etch rates relative to PS and PMMA (silicon dioxide excitation electrode) are displayed. The etch rates of PMMA are much faster than those of PS and both decrease in the order $CF_4 > CF_3Cl > CF_3Br$, proportionally to the amount of fluorine in the discharge (*Figure 1a*). The formation of volatile fluorocarbons is considered the driving force of etching for polymers[14,15].

When the carbon electrode is used, deposition is observed for all gases. Of course, at equilibrium the deposition rate is the same on PS and PMMA and increases in the order $CF_4 < CF_3Cl < CF_3Br$. This trend parallels the increase, in the same order, in the amount of halocarbon radicals, as observed by actinometry (*Figure 1b*).

Etching and polymerization versus ion bombardment

Etching and deposition rates can also be tuned by altering the energy of ions bombarding the sample in the plasma[14]. This can be achieved by using an r.f. induced self-bias voltage. In our apparatus[18,26,27] the plasma potential is about +20 V, so that the maximum ion energy is the sum of the bias voltage plus 20 eV. Most of the ions have this energy. In fact, the transit time for the ion to traverse the sheath is longer than the period of the r.f. (13.56 MHz), so that the ions time average the r.f. voltages[23]. Furthermore, ion–neutral collisions in the sheath are negligible at the operating pressure (10 mTorr).

Using the carbon excitation electrode, the effect of ion bombardment was to reduce the deposition rate with increasing bias voltage, finally turning the reaction into etching. The bias voltages necessary to stop deposition are reported in *Table 1* and increase in the order $CF_4 < CF_3Cl < CF_3Br$, again in agreement with the number of halocarbon radicals present in the discharge (*Figure 1b*).

With QCMs we obtained the etch rates of PS and PMMA for CF_4, CF_3Cl and CF_3Br discharges as a function of bias voltage using a silicon dioxide excitation electrode. In both cases a linear increase of etch rate with ion bombardment was observed, as shown in *Figure 4*. At all voltages the etching efficiency is in the order $CF_4 > CF_3Cl > CF_3Br$, for both PS and PMMA, in agreement with the amount of fluorine detected by actinometry (*Figure 1a*).

In *Figure 5* the etch rate ratios of the different gases are plotted *versus* bias voltage with the aim of comparing the relative etching efficiency of the gases. As shown in *Figure 5(a)*, the ratios between etch rates obtained with different gases but at the same bias voltage are fairly constant. This suggests a similar kinetic dependence of etch rate on bias voltage for all gases.

For PS the etch rate increases linearly with bias voltage. But it appears that the CF_4/CF_3Cl and CF_4/CF_3Br etch rate ratios decrease with increasing bias voltage (*Figure 5b*), suggesting that at higher bias voltages CF_3Cl and CF_3Br discharges become more efficient. It can also be argued that in these cases the kinetic relationship between etch rate and bias voltage in CF_4 discharges differs from that in CF_3Cl and CF_3Br discharges. In fact, the ratio of CF_3Cl to CF_3Br etch

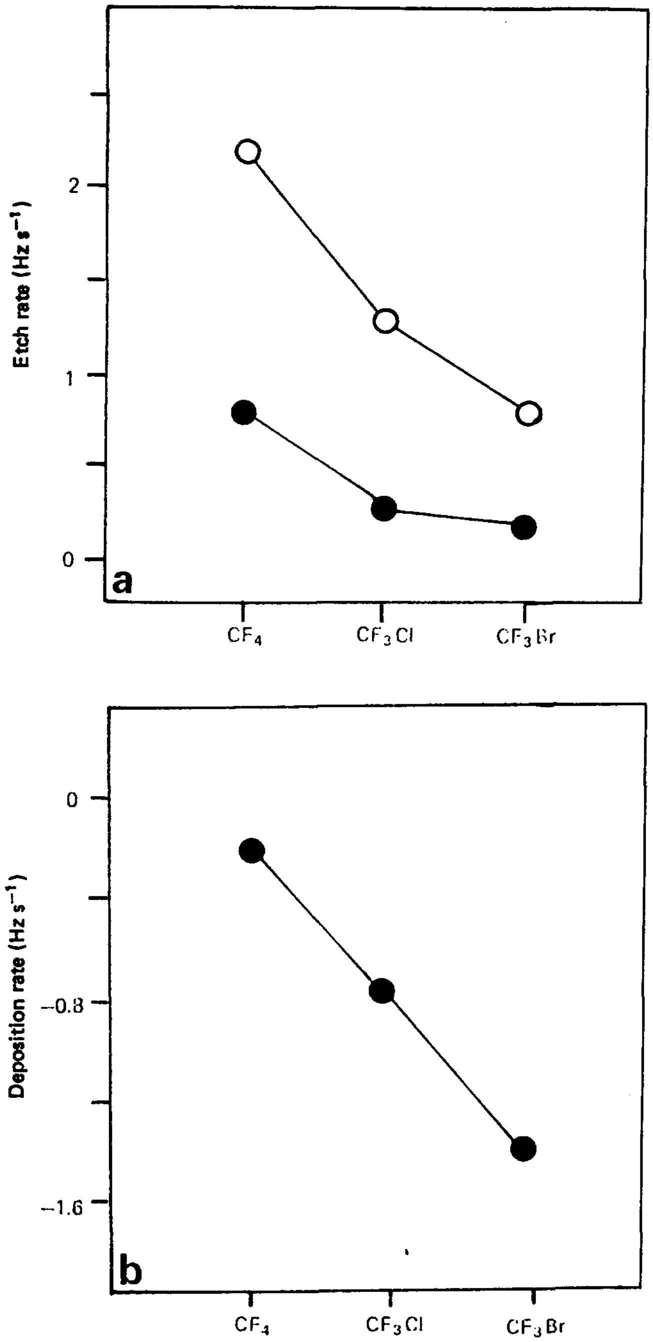

Figure 3 (a) Etch rates of PS (●) and PMMA (○) by halofluorocarbon discharges (SiO_2 excitation electrode, grounded sample). (b) Deposition rate on PS and PMMA by halofluorocarbon discharges (pyrolitic carbon excitation electrode, grounded sample)

Table 1 Bias voltages needed to turn deposition into etching (carbon excitation electrode, data relative to PMMA)

Gas	Bias voltage (V)
CF_4	−20
CF_3Cl	−60
CE_3Br	−100

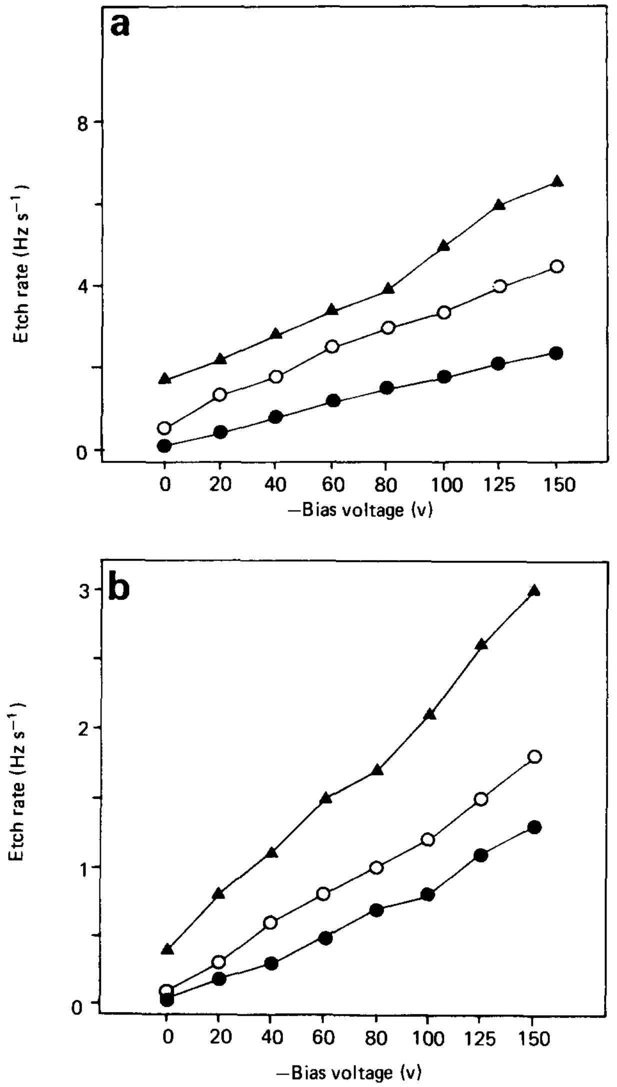

Figure 4 (a) Etch rates of PS by halofluorocarbon discharges (SiO_2 excitation electrode). (b) Etch rates of PMMA by halofluorocarbon discharges (SiO_2 excitation electrode). ▲, CF_4; □, CF_3Cl; ●, CF_3Br

rates is constant, suggesting that the changes in discharge chemistry obtained by the introduction of chlorine and bromine have the same effect on PS etch rates. Most likely the presence of aromatic rings in PS has some influence on these behaviours.

Derivatization

The extent of derivatization was studied using X.p.s., a surface sensitive spectroscopy. The specimen shapes and dimensions and the fact that only shallow layers are modified prevented us from using more structure sensitive probes, such as vibrational spectroscopies. Scanning electron microscopy (SEM) studies did not show significant alterations in surface roughness as a consequence of the treatment.

X.p.s. gives information about the grafting of halogens and halogen containing groups on the polymer surfaces and, for PMMA, about the depletion of oxygen containing functions as a consequence of the treatment. Unfortunately, it was impossible to assess the extent of destruction of the aromatic ring in PS, since the introduction of fluorine produces features in the C-1s spectrum which overlap the shake-up region.

We studied surface composition changes after discharges obtained with the silicon dioxide excitation electrode, to prevent deposition of plasma polymer. No bias voltage was applied on the sample, to maximize the effect of derivatization with respect to etching. In *Table 2* the F/C, Cl/C and Br/C ratios are presented for both PS and PMMA. For PMMA the O/C ratios after the treatment are also presented. The O/C ratio for plain PMMA is 0.40; for untreated PMMA we found 0.35, due probably to some hydrocarbon contamination. Therefore, the treatment appears to cause a strong reduction in the oxygen concentration at the surface, without strong differences among the different gases. As expected, the highest F/C ratio has been observed following CF_4 treatments. Interestingly, the F/C ratio is higher for CF_3Br than for CF_3Cl treatment, while the actinometric F/Ar ratio is higher for the CF_3Cl discharge (*Figure 1a*). A less efficient competition with fluorine or bromine with respect to chlorine, due to steric and electronic effects, can explain this seeming contradiction.

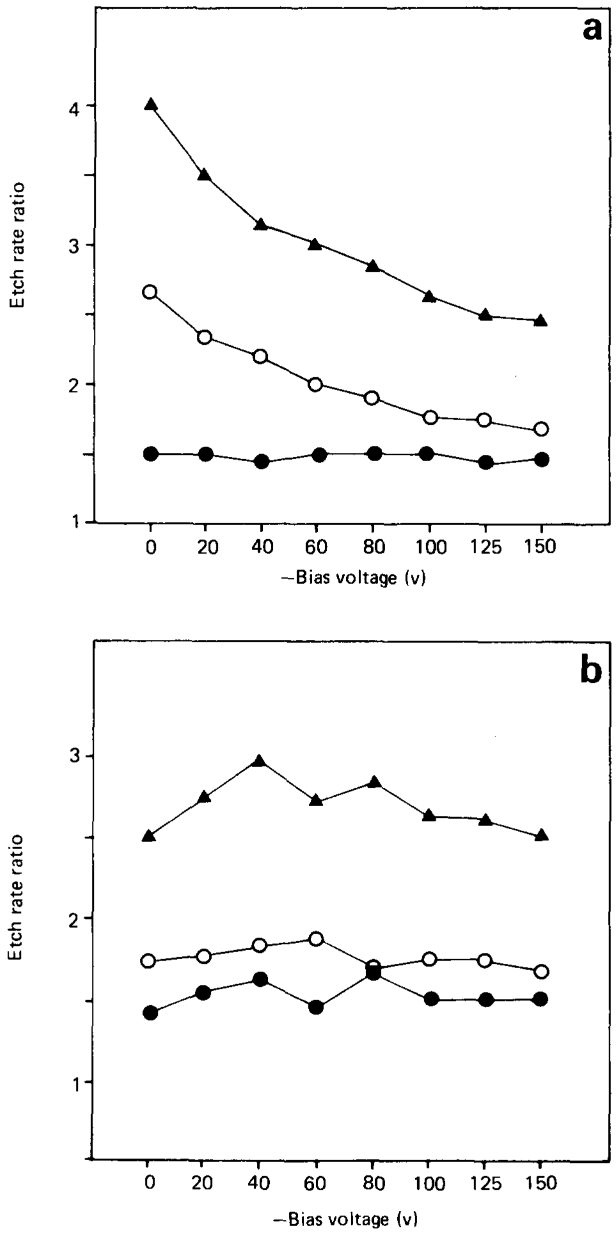

Figure 5 QCM etch rate ratios for (a) PMMA and (b) PS: CF_4/CF_3Cl (○), CF_4/CF_3Br (▲), CF_3Cl/CF_3Br (●)

Table 2 X.p.s. X/C ratios (X=F, Cl, Br, O) after CF_4, CF_3Cl and CF_3Br plasma treatments

Polymer	Gas	F/C	Cl/C	Br/C	O/C
PS	CF_4	0.69	–	–	–
	CF_3Cl	0.33	0.27	–	–
	CF_3Br	0.40	–	0.13	–
PMMA	CF_4	0.67	–	–	0.22
	CF_3Cl	0.28	0.17	–	0.19
	CF_3Br	0.35	–	0.08	0.21
	Untreated	–	–	–	0.35

Generally, the X/C ratios (X = F, Cl, Br) are higher in PS than in PMMA. A different behaviour of F from that of Cl and Br is evident. In treated PS the F/C ratios are less than 20% higher than in PMMA, while the Cl/C and Br/C ratios are about 60% higher. This result might be related, together with the preferential enhancement of CF_3Cl and CF_3Br etch rates by ion bombardment, to the interaction of species formed in the latter discharges, in particular halogen molecules, with the aromatic ring.

Line-fitting of the XPS C-1s peaks provided some more useful information. In *Figure 6* the deconvoluted C-1s peaks of PS treated with CF_4 and CF_3Cl plasma are shown. Clark[28] and Briggs[29] performed a lot of work in the assignment of binding energy shifts to particular bonding situations. In our case the assignment of the components at highest binding energy is fairly unambiguous: the one at 8.5 eV from the main hydrocarbon peak is relative to CF_3 groups, while that at 6.5 eV is relative to CF_2 groups. The components at 4.4, 3.6 and 2.8 eV from the main peak are probably relative to CF and/or CCl_x, CBr_x (x=2, 3) groups in different bonding situations, and those at about 1.6 eV from the main peak are probably relative to C–CF and C–Cl and C–Br groups[28,29]. For PMMA the components relative to CF and C–CF groups have binding energies close to C–O and O–C=O groups. The best fit was obtained using only two components relative to CF and CCl_x, C–Br_x groups, at 3.8 and 4.5 eV from the main peak, and one due to C–CF, C–Cl, C–Br groups, at 1.6 eV from the hydrocarbon peak. Of course, the components shifted by 1.6 and 3.8 eV account for C–O and O–C=O groups as well.

In *Figure 7* the ratios of the various components to the main hydrocarbon peak at plotted. For PMMA (*Figure 7a*), the components at 1.6 and 3.8 eV are due to the presence of CF, CCl_x, CBr_x and CO contributions. There is not much difference between CF_4 and other plasma treatments. The change is remarkable for the strongly shifted components: their intensity is much higher for the CF_4 plasma treated sample. This effect can be related to the discharge chemistry of CF_3Cl and CF_3Br plasmas, leading to enrichment in chlorine and bromine containing species, as shown in the mass spectra plotted in *Figure 2*(*b*) and (*c*).

The change is even more pronounced for PS (*Figure 7b*). The CF_4 plasma treated sample exhibits a strong presence of CF–CF_2, CF_2, CF_3 groups, pointing to the grafting of fluorocarbon monomers and oligomers to the active sites created by the high energy density medium. In CF_3Cl and CF_3Br treated samples the most intense components are those with lower shifts, due probably to the high abundance of Cl and Br containing radicals in the plasma, which again graft to active sites on the PS surface. Furthermore, molecular chlorine and bromine can interact with the aromatic ring, leading again to CCl_x and CBr_x groups, thereby enhancing the components with low binding energy shifts. The latter reaction is absent in PMMA and there is no clear difference in the relative intensity of components with low shifts.

DISCUSSION AND CONCLUSION

Our experiments showed that the tendency of halofluorocarbon discharges to give etching or polymerization on polystyrene and poly(methyl methacrylate) can be tuned by altering the discharge chemistry and the energy of positive ions hitting the sample. Etching can be enhanced by increasing the halogen/halofluorocarbon radical ratios by, for example, using different excitation electrodes. In both PS and PMMA, etch rates are also increased by applying negative bias voltages on the sample.

Actinometric studies showed that the amount of atomic fluorine in the discharge decreases in the order $CF_3Br < CF_3Cl < CF_4$, the same trend as for etch rates. Halocarbon radicals are present when the carbon excitation electrode is used and their relative amount, as observed by actinometry, is in the order $CF_3Br > CF_3Cl > CF_4$, the same trend as for deposition rates. By mass spectroscopy we also found that while in the CF_4 discharge essentially CF_x^+ fragments are present, in CF_3Cl and CF_3Br plasma fragments like Cl^{2+}, Br^{2+}, $CFCl^{2+}$ and $CFBr^{2+}$ are present (*Figure 2*). The complex discharge chemistry is probably triggered by the consumption of fluorine in the etching of the target, leading to a discharge rich in

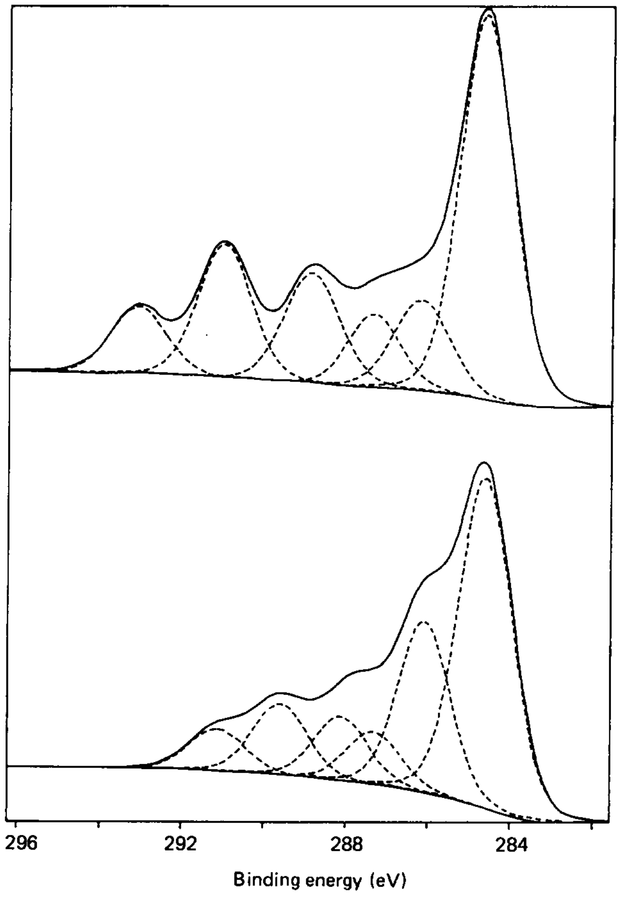

Figure 6 Line-fitted X.p.s. C-1s spectra of PS treated with CF_4 (top) and CF_3Cl (bottom) plasmas

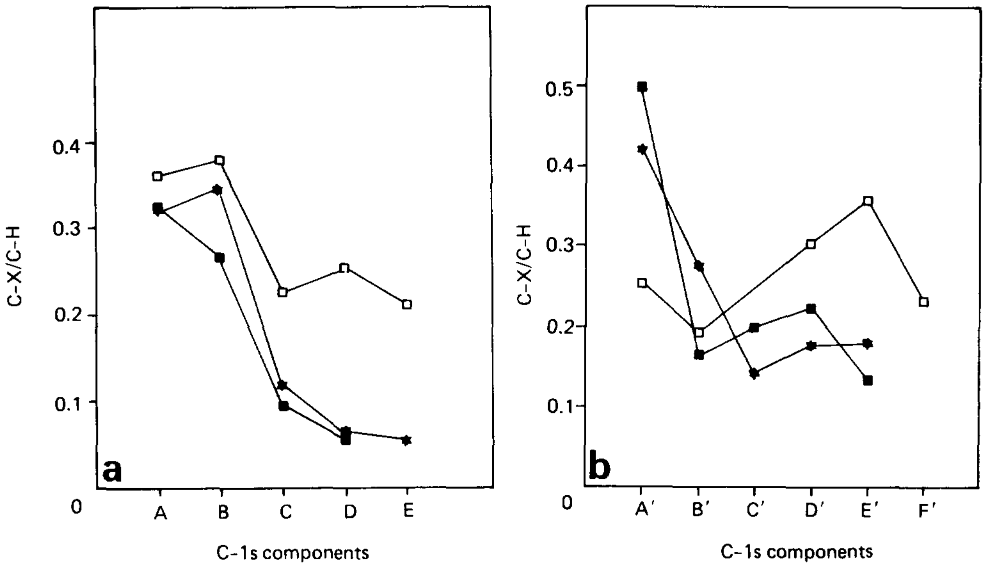

Figure 7 (a) Ratio of the intensity of C-1s components relative to C–X groups to the main hydrocarbon peak for (a) PMMA and (b) PS treated with CF_4 (□), CF_3Cl (■) and CF_3Br (*) plasmas. A, C–CF, C–O, C–Cl. CBr2, etc.; B, CF, CCl2, O–C=O, etc.; C, CF–CF2, O–C–F; D, CF2; E, CF3. A', C–CF, C–Cl, CBr2, etc.; B', CF; C', CCl2, CFBr; D', CF–CF2, CFCl; E', CF2; F', CF3

chlorine and bromine containing radicals and also in chlorine and bromine molecules.

Ion bombardment not only introduces energy into the polymer, thereby stimulating linear increases in etch rates, but also enhances chemical reactions selectively. In CF_3X plasmas a comparable kinetic dependence of PMMA etch rates on bias voltage has been found, as shown by the constancy of the ratios between the etch rates of CF_4, CF_3Cl and CF_3Br. In PS a decrease in the CF_4/CF_3Cl and CF_4/CF_3Br etch rate ratio with increasing bias voltage was observed. The kinetic dependence of CF_3Cl and CF_3Br etch rates on bias voltage is changed. Ion bombardment might enhance the interaction of halogen molecules present in the discharge with the aromatic ring, inducing selective enhancement in their etch rate.

As to derivatization, it has been shown that halogen atoms are grafted to the PS surface more easily than to PMMA. Furthermore, the introduction of Cl and Br is enhanced more effectively than that of F, due probably both the presence of aromatic rings in PS and of molecular chlorine and bromine in the CF_3Cl and CF_3Br discharges. In particular, the study of the components of C-1s peaks showed that in PS treated with CF_3Cl and CF_3Br plasmas there is a strong enhancement of components due to CCl_x and CBr_x groups, while the CF_4 treated sample is rich in CF_2 and CF_3 groups. In PMMA the trend is less pronounced, pointing again to the interaction of the aromatic ring with halogen molecules as an effective way of introducing Cl and Br at the polymer surface.

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REFERENCES

1 Hollahan, J. R. and Bell, A. T. (Eds) 'Techniques and Applications of Plasma Chemistry', Wiley, New York, 1974
2 Clark, D. T. and Feast, W. J. (Eds) 'Polymer Surfaces', Wiley, New York, 1978
3 Havens, M.R., Biolsi, M. E. and Mayhan, K. G. *J. Vac. Sci. Technol.* 1976, **13**, 575
4 Westerdahl, C. J., Hall, J. R., Schramm, E. C. and Levi, D. W. *J. Coll. Interface Sci.* 1974, **47**, 610
5 Moran, J. M. and Maydan, D. *J. Vac. Sci. Technol.* 1979, **16**, 1620
6 Reichelderfer, R. F., Welty, J. M. and Battey, J. F. *J. Electrochem. Soc.* 1977, **124**, 1926
7 Corbin, G. A., Cohen, R. E. and Baddour, R. F. *Macromolecules* 1985, **18**, 98
8 Anand, M., Baddour, R. F. and Cohen, R. E. U.S. Patents 4 264 750, 1981; 4 404 256, 1983
9 Hall, T. M., Wagner, A. and Thompson, L. F. *J. Appl. Phys.* 1982, **53**, 3997
10 Clark, D. T. and Dilks, A. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 957
11 Taylor, G. N., Wolf, T. M. and Stillwagon, L. E. *Solid State Electron.* 1984, **27**(2), 145
12 Harada, K. *J. Appl. Polym. Sci.* 1981, **26**, 1961
13 Wu, B. J., Hess, D. W., Soong, D. S. and Bell, A. T. *J. Appl. Phys.* 1983, **54**, 1725
14 Coburn, J. W. *Plasma Chem. Plasma Process.* 1983, **2**, 1
15 Flamm, D. L. and Donnelly, V. M. *Plasma Chem. Plasma Process.* 1981, **1**, 317
16 Yagi, T., Pavlath, A. E. and Pittman, A. G. *J. Appl. Polym. Sci.* 1982, **27**, 4019
17 Strobel, M., Corn, S., Lyons, C. S. and Korba, G. A. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1125
18 Koehler, K., Coburn, J. W., Horne, D. E., Kay, E. and Heller, J. H. *J. Appl. Phys.* 1985, **57**, 59
19 Kay, E., Coburn, J. W. and Kruppa, G. *Le Vide* 1976, **183**, 89
20 'Handbook of X-Ray Photoelectron Spectroscopy', Perkin–Elmer Physical Electronics Division, 1979
21 d'Agostino, R., Capezzuto, P., Bruno, G. and Cramarossa, F. *Pure Appl. Chem.* 1985, **57**, 1287
22 Coburn, J. W. and Chen, M. *J. Appl. Phys.* 1980, **51**, 3134

23 d'Agostino, R., Cramarossa, F., De Benedictis, S. and Ferraro, G. *J. Appl. Phys.* 1981, **52**, 1259

24 Coburn, J. W. *Rev. Sci. Instr.* 1970, **41**, 1219 and references therein

25 Coburn, J. W. and Kay, E. *J. Appl. Phys.* 1972, **43**, 4965

26 Us, N. C., Sadowski, R. W. and Coburn, J. W. *Plasma Chem. Plasma Process.* 1986, **6**, 1

27 Fracassi, F., Occhiello, E. and Coburn, J. W. *J. Appl. Phys.* 1987, **62**, 3980

28 Clark, D. T. in 'Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy' (Ed. D. Briggs), Heyden, London, 1977, p. 226

29 Briggs, D. in 'Practical Surface Analysis' (Eds D. Briggs and M. P. Seah), Wiley, Chichester, 1983, p. 374