

## Plasma etching and modification of organic polymers

Frank D. Egitto

Systems Technology Division, IBM Corporation, Endicott, NY USA

**Abstract** - Etching and modification of polymers by plasmas is discussed in terms of the roles played by atomic and molecular oxygen, atomic fluorine,  $CF_x$  radicals, ions, high energy metastable species, and photons. Addition of fluorine-containing gases to oxygen can increase both O atom densities in the plasma and polymer etching rates. The etching rate behavior generally exhibits a maximum at a specific concentration of this additive. Process parameters which alter the concentrations of O and F atoms in the plasma or affect the rate of delivery of these species to the polymer surface shift the position of this maximum with respect to feed gas composition. However, the gas composition which yields maximum rates exhibits a strong dependence on polymer structure, specifically, its degree of unsaturation. This is explained on the basis of molecular orbital (MO) arguments which predict that the surfaces of unsaturated polymers have a higher affinity than saturated polymer surfaces for atomic fluorine. Favored reaction pathways leading to volatile etching products are proposed based on MO calculations of relative bond strengths for various oxygenated and fluorinated organic model compounds. Although fluorine abstraction of hydrogen plays a major role in generating radical sites on saturated polymer surfaces, it is likely that etching of unsaturated moieties proceeds through a saturated radical intermediate resulting from addition reactions of fluorine atoms. Excessive amounts of fluorine in the plasma result in reduced etching rates and incorporation of fluorine and/or  $CF_x$  radicals into the polymer. Polymer film surfaces are also modified by high energy metastables and ultraviolet radiation generated from noble gas plasmas. The effect of vacuum ultraviolet radiation from helium microwave plasmas on films of polytetrafluoroethylene and polyethylene is addressed.

### INTRODUCTION

A cursory survey of the literature will reveal that non-local thermal equilibrium (cold) plasmas are being used with increasing frequency for wide ranging applications related to polymer etching and surface modification. Several reviews have recently been published (ref. 1 to 4). The nature of polymeric materials makes mechanistic studies of etching and modification processes complex. Contrast, for example, the relatively simple structure of mono-crystalline silicon with that of polymeric materials which contain C, H, N, O, F, Br, Cl, or S arranged in a variety of functional groups and repeating units, in chains of various molecular weight. Free radicals, excited and ground state neutrals, ions and photons can each contribute to etching and modification processes, often with combined and synergistic effects. This paper is largely a review, albeit brief, of plasma interactions with polymers. An attempt has been made to look for trends in etching behaviors and to deconvolute the effects of various processing parameters and polymer structures.

### OXYGEN PLASMAS

Polymeric materials are chosen for a particular application based on their chemical, mechanical and/or electrical characteristics. Oxidative degradation has long been a leading detractor of polymer performance. This has led to a number of studies addressing mechanisms which accelerate degradation such as thermally enhanced oxidation and photo-oxidation effects, and recently, the effect of atomic oxygen in low Earth orbit (LEO) (ref. 5). Use of oxygen-containing plasmas for polymer processing is now widespread in the electronics industry. The earliest reports by Irving (ref. 6) discussed the use of oxygen plasmas to remove photoresist from integrated circuits. Today, sub-micron features can be transferred into polymer films several microns thick, with anisotropic etching processes, to form high-resolution lithographic masks with multilayer resist schemes (ref. 7 to 10). Oxygen plasmas are also used to modify polymer surfaces to improve wettability or bondability to other materials (ref. 11 to 14).

With oxygen free radical chemistry, the distinction between polymer etching (material removal) and modification is somewhat artificial. The two processes typically occur simultaneously and distinction is usually a matter of degree of material removal or by virtue of the particular application (e.g., pattern delineation or change in wettability). However, the mechanisms involved can be treated simultaneously.

Ignoring, for now, the role of ions and photons in oxygen plasmas, it is clear that atomic oxygen free radicals initiate the etching process. This has been demonstrated by the linear relationship between etching rates and either O atom concentration in the plasma (ref. 15) or the amount of O atoms consumed during polymer etching (ref. 16). Although singlet oxygen is known to react without catalyst, it has been reported that polystyrene is unaffected by this constituent of oxygen plasmas (ref. 17). Oxygen atom attack of a polymer can proceed by a variety of mechanisms including abstraction:



addition to unsaturated moieties (ref. 18 & 19):



or by absorption of the O<sub>2</sub> dissociation energy (ref. 20):



One might anticipate that polymer radical site formation will affect bond strengths in polymers. A technique used by Cain, et al. (ref. 21) to compare relative bond energies employed molecular orbital (MO) calculations at the Extended Huckel level (ref. 22) on model polymer structures. For example, ethane and ethane derivatives are used to represent saturated polymers, and ethylene and its derivatives represent unsaturated polymers. Overlap populations, which reflect the degree of bonding between two atoms in a compound, are calculated and compared. Results for ethane, ethylene, and associated radicals are given in Table 1.

Table 1. Carbon-carbon bond overlap populations for ethane, ethylene and associated radicals (after ref. 22).

Structure	Overlap Population
CH <sub>3</sub> -CH <sub>3</sub>	0.72
$\dot{C}H_2$ -CH <sub>3</sub>	0.76
CH <sub>2</sub> =CH <sub>2</sub>	1.29
$\dot{C}H=CH_2$	1.32
$\dot{C}H_2$ -CH <sub>2</sub> O	0.78
$\dot{C}H_2$ -CH <sub>2</sub> F	0.75

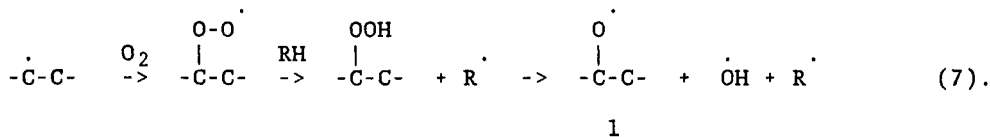
Table 2. Carbon-carbon bond overlap populations for oxygenated derivatives of ethane and ethylene.

Structure	Overlap Population
$\dot{C}H_2O$ -CH <sub>3</sub>	0.54
CHO=CH <sub>2</sub>	1.10
CH <sub>2</sub> O-CH <sub>2</sub> O	0.39
$\dot{C}H_2O$ -CH <sub>2</sub> F	0.55

Table 3. Carbon-carbon bond overlap populations for fluorinated ethane and ethylene.

Structure	Overlap Population
CH <sub>2</sub> F-CH <sub>3</sub>	0.73
CHF=CH <sub>2</sub>	1.28
CH <sub>2</sub> F-CH <sub>2</sub> F	0.74

For O atom reactions, abstraction does not result in bond weakening for either saturated or unsaturated compounds. Only addition of oxygen to the unsaturated molecule, leading to a saturated radical, results in a weakened C-C bond. Not surprisingly, the resulting bond energy is on the order of the C-C bond in ethane. It appears likely that subsequent attack of the radical site is required for bond breaking or chain scission which can lead to low molecular weight volatile fragments. Hansen, et al. (ref. 11) have outlined a possible autoxidation process:



Overlap populations of various oxidized derivatives, 1, of model compounds are shown in Table 2. Significantly weakened bonds are now evident. From these structures, scission processes can occur leading to volatile etch products (such as CO and CO<sub>2</sub>):



Taylor and Wolf (ref. 23) measured the relative etching rates of forty polymers in oxygen plasmas. They reported that strong backbone bonds, aromatic and polar functional groups, and metallic atoms decrease removal rates. Moss and coworkers (ref. 12 & 24) have proposed that stability of aromatic polymers against etching in oxygen plasmas can possibly be due to addition reactions of oxygen atoms with aromatic rings to form phenols, without formation of free radicals.

X-ray photoelectron spectroscopy (XPS) has been used extensively to characterize the surfaces of polymer films exposed to oxygen plasmas (ref. 18, 19, 25 to 28). This technique probes the top 3 to 5 nm of the surface. C 1s XPS spectra of three polymers exposed downstream from an oxygen microwave plasma are compared with spectra for the untreated films in Fig. 1 (ref. 28). In general, surfaces become oxidized upon exposure. Advancing deionized (DI) water contact angles decreased with treatment from 95, 91, and 70 degrees to 18, 12, and 12 for low density polyethylene (PE), polyetheretherketone (PEEK) and polyimide (PI), respectively. Of the three polymers, PE showed the least amount of oxidation (12 atomic %, compared to 37% and 30% for PEEK and PI, respectively), probably due to a higher degree of removal for PE than for the aromatic polymers (ref. 23). The decrease in the  $\pi \rightarrow \pi^*$  shake-up peak around 291 eV for treated PEEK films is indicative of loss of aromaticity. Treatment of both PEEK and PI results in a large increase in carbonyl groups (288.1 eV). Additional peaks for treated PI have been attributed to acid or ester groups (288.6 eV) and polycarbonate or peroxy groups (289.9 eV) (ref. 25).

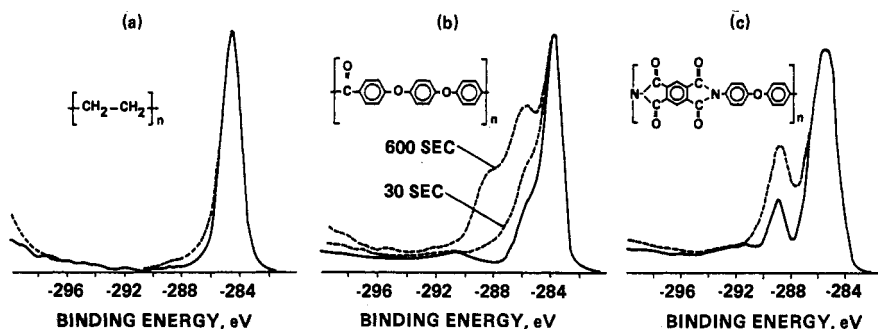


Fig. 1. Comparison of C 1s XPS spectra for polymers before and after treatment downstream from an oxygen microwave plasma; (a) PE, (b) PEEK, (c) PI (PMDA-ODA) (after ref. 28). Spectra for treated films are shown as dashed lines. Treatment times were ten minutes, except where indicated.

Hansen and coworkers (ref. 11) observed that O atom producing plasmas could be used to improve wetting of polymer surfaces. This presumably resulted from formation of C=O, OH, and -COOH groups. DI water contact angle on polyimide surfaces is shown as a function of power level and treatment time downstream from an oxygen microwave plasma in Fig. 2. In this experiment, relative O atom number density in the plasma, measured using optical emission

spectroscopy with an argon actinometer, increased linearly with power. The initial rapid decrease in contact angle does not exhibit a pronounced dependence on power level (i.e., O atom concentration), indicative of an initial fast reaction. This appears to be followed by a second, slower reaction which exhibits a dependence on O atom concentration. Katnani, et al. (ref. 29) have reported an increase with time in the intensity of the C 1s peak attributed to C=O on surfaces of polyimide treated with oxygen plasma and have demonstrated a correlation between the increase in this peak and the adhesion of subsequently deposited metal films to the treated polyimide surface.

One means of increasing O atom densities in the plasma and, as a result, increase rates of polymer etching and modification, is by addition of N<sub>2</sub> (ref. 30) or N<sub>2</sub>O (ref. 31) to the O<sub>2</sub> gas feed. Although these additives increase O atom concentrations, surface mechanisms probably are not changed; N<sub>2</sub>O addition did not produce a change in activation energy associated with etching when compared with etching using pure oxygen (ref. 31). Addition of small amounts of nitrogen to oxygen plasmas can also serve to increase the rate of surface modification, as measured by DI water contact angles, shown in Fig. 2.

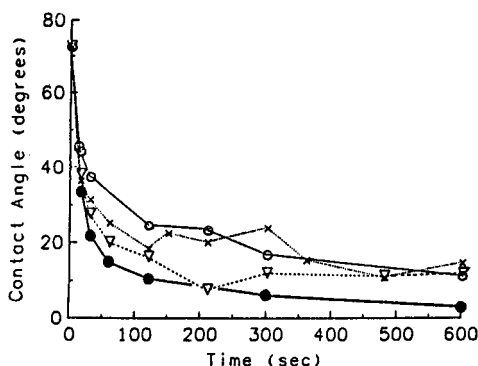


Fig. 2. Advancing D.I. water contact angle on surfaces of polyimide films versus time of treatment downstream from O<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> microwave (MW) plasmas at various levels of absorbed MW power; o, x, and ∇ correspond to 30, 60, and 120 watts, respectively, oxygen plasma; • indicates 60 watts, 15% nitrogen in oxygen.

Typically, etching rates in plasmas of pure oxygen are low when compared with rates obtained by addition of small amounts of fluorine-containing gases (see below). Significant increases in etching rate in pure oxygen plasmas can be obtained at elevated temperatures or when etching is performed with the assistance of ion bombardment. The effects of ions and other energetic species generated in the plasma is discussed in more detail below.

#### ADDITION OF FLUORINE-CONTAINING GASES

Addition of fluorine containing gases, such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, SF<sub>6</sub>, and NF<sub>3</sub> are also known to increase O atom concentrations relative to those obtained in pure O<sub>2</sub> plasmas. The kinetics of gas phase reactions leading to the formation of O and F atoms in the plasma has been modelled for mixtures of O<sub>2</sub> and CF<sub>4</sub> by Plumb and Ryan (ref. 32). Atomic oxygen production is enhanced primarily through electron-induced dissociation processes. It appears that the major role of fluorinated gas addition in increasing O atom densities in the plasma is by increasing the number density and/or energies of electrons in the plasma. Indeed, Kushner (ref. 33) has shown that electron densities increase with addition of CF<sub>4</sub> to O<sub>2</sub>. As mentioned above, increased O atom densities alone will result in increased polymer etching rates. However, fluorine can serve to generate polymer radical sites via reactions analogous to those listed above for O atoms, i.e., abstraction:



or addition reactions with unsaturated polymers:



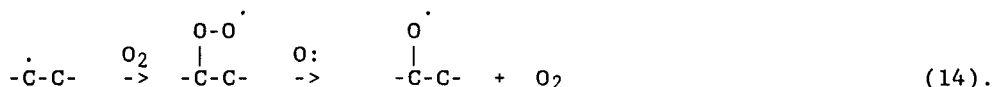
Using the approach outlined above for reactions of O atoms with polymers, Cain, et al. (ref. 21) have calculated overlap populations for radicals generated in model compounds via reactions (9), (10), and (12) above. These are also shown in Table 1. Fluorine abstraction of hydrogen does not weaken C-C or C=C bonds. Although addition reactions of fluorine to C=C serves to significantly weaken the bond, again the resulting saturated radical intermediate is no weaker than the C-C bond of ethane.

Reactions (7) and (8) subsequent to radical generation via reactions (9) through (12) can lead to volatile etch products. But what of the relative importance of O atoms versus oxygen molecules in attack of polymer radicals and subsequent chain scission? Golub, et al. (ref. 5) have proposed that the significantly higher uptake of oxygen by polyimide exposed in an rf plasma reactor when compared with exposure in LEO was because the ratio O<sub>2</sub>/O is two orders of magnitude greater in the plasma system. Occhiello, et al. (ref. 34) reached a similar conclusion regarding the relative importance of O<sub>2</sub> and O for oxidation and etching of polycarbonate.

One might anticipate that the relative importance of oxygen atoms and molecules is some function of the polymer structure. Indeed, Mugica, et al. (ref. 35) have proposed that the dramatically higher etch rate of polyvinylalcohol (PVA) in O<sub>2</sub>/CF<sub>4</sub> plasmas, when compared to several other polymers, including polyethylene, was due to the reaction of O<sub>2</sub> with radicals produced from the abstraction of H atoms by O and F atoms. In general, however, it is not totally clear whether the oxidized radical precursor to the alkoxy degradation reaction (8) is formed as outlined in reaction (7), by reaction with O, according to



or by some series of reactions with O<sub>2</sub> and O, for example



The position of the etching rate maximum for a given polymer has been shown to exhibit a strong dependence on the ratio of concentrations of atomic oxygen and fluorine in the plasma (ref. 25 & 36). Since reactions (9-12) occur at a much higher rate than reactions (1-6), the dependence on O atom concentration might be the result of reactions such as (13) and (14).

Comparing the overlap populations for CHO=CH<sub>2</sub> (1.10) and CH<sub>2</sub>O-CH<sub>2</sub>F (0.55) radicals in Table 2, it appears that although abstraction of hydrogen from saturated polymers by fluorine with subsequent oxidation (via reaction with O<sub>2</sub> or O) leads to bond breaking and formation of volatile products, for unsaturated polymers the preferred pathway may be an addition reaction with fluorine leading to a saturated radical intermediate, followed by oxidation. Chain scission can then proceed via (8).

Fluorine present in excess (e.g., high concentrations of CF<sub>4</sub> in O<sub>2</sub>) results in fluorination according to



or



Table 3 lists overlap populations for C-C and C=C bonds for the fluorinated ethane and ethylene derivatives. Stable fluorinated products result in high concentrations of fluorine on polymer surfaces treated with plasmas rich in fluorine (ref. 25 & 37 to 42). Fluorine atoms in high concentrations can compete with O<sub>2</sub> or O atoms for polymer radical sites and retard etching rates. A proper balance between etching enhancement (via F addition and abstraction reactions) and polymer fluorination is required to achieve maximum etching rates. For a given concentration of atomic oxygen in the plasma, there is an optimum amount of fluorine for which maximum etching rates will be achieved (Fig. 3a).

Fluorination of polymers can proceed either via grafting of fluorine atoms or  $CF_x$  radicals. Strobel, et al. (ref. 43) used XPS to study the fluorination of polyethylene (PE) and polypropylene (PP) films exposed to  $SF_6$ ,  $CF_4$ , and  $C_2F_6$  plasmas. It was observed that  $SF_6$  bonded F atoms to the surface,  $CF_4$  fluorination was dominated by F atom bonding, and fluorination with  $C_2F_6$  was dominated by  $CF_x$  radicals. There was no deposition of plasma-polymerized films. Occhiello, et al. (ref. 34) proposed that for 1%  $O_2$  in  $CF_4$ , fluorination of polycarbonate was dominated by grafting of  $CF_x$  radicals, while at higher  $O_2$  concentrations F atom grafting dominated. Van Ooij and Michael (ref. 44) used XPS and SSIMS to characterize surfaces of PP and polystyrene (PS) films fluorinated using  $SF_6$  and  $C_2F_6$  plasmas. For both polymers, fluorination with  $SF_6$  was dominated by F atom grafting. With  $C_2F_6$ , more incorporation of  $CF_x$  radicals takes place. In addition,  $SF_6$  showed much more aggressive attack of the phenyl groups in PS than did  $C_2F_6$  plasmas.

The depth of polymer fluorination has been measured by various techniques for a variety of polymers. These studies are summarized in Table 4. The depths reported are much greater than the depth of oxidation obtained after long exposures of polyimide to microwave-generated oxygen plasmas, less than 0.3 nm, as measured using angle resolved XPS, infrared (IR) spectroscopy and Rutherford backscattering spectroscopy (RBS) (ref. 28). This is probably due to simultaneous removal and oxidation of the polymer with oxygen plasmas. The fluorinated polymer surface is highly resistant to etching in the absence of ion bombardment (ref. 40 to 42). In addition, fluorination of polymers tends to decrease their surface energies (ref. 45 & 46).

Table 4. Depth of fluorination for various polymers.

Polymer	Gases	Plasma System	Measurement Technique	Fluorine Depth (nm)	Fluorine Profile	Ref.
PE	$F_2$	Barrel w/Faraday cage	Angle Res. XPS and Microbalance	48	Diffusion controlled	37
PMMA	$CF_4/O_2$	Barrel w/Faraday cage	Differential etch rates in $O_2$ plasma, fluorinated surface layer versus non-fluorinated	75	Step Function	38
Butvar				50-420		
Novolac				190		
Novolac	$CF_4/O_2$	Planar Diode		1000	Diffusion (F ion) controlled	39
PI	$CF_4/O_2$	Downstream Microwave	XPS and RBS	60	Diffusion controlled	41

Several factors affect the optimum ratio of oxygen and fluorine atoms in the gas required to achieve the maximum etching rate. For a given polymer, the position of the maximum can vary with amount of etchable material (ref. 36), reactor wall conditions and system geometry (ref. 40). The relative ease with which fluorine and oxygen atoms approach the surface of polymers (surface affinity) also affects the amounts required in the gas. This affinity of free radicals for various surfaces is a function of polymer structure and surface temperature. For example, polymers for which the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is large will exhibit a low affinity for fluorine atoms (a more repulsive potential). For polymers with a small HOMO-LUMO energy differential, a higher affinity for fluorine atoms exists. In general, the HOMO-LUMO gap is larger for saturated polymers than for unsaturated polymers. As a result, saturated polymers require more fluorine in the gas (typically higher concentrations of  $CF_4$ ,  $SF_6$ , etc.) to achieve maximum etching rates than do unsaturated polymers. This behavior is demonstrated in Fig. 3b.

The affinity of fluorine for polymer surfaces can decrease with increasing temperature. Robinson and Shivashankar (ref. 48) have demonstrated that a greater concentration of  $CF_4$  in  $O_2$  is required to achieve maximum etch rates for polyimide at 70°C than at 20°C.

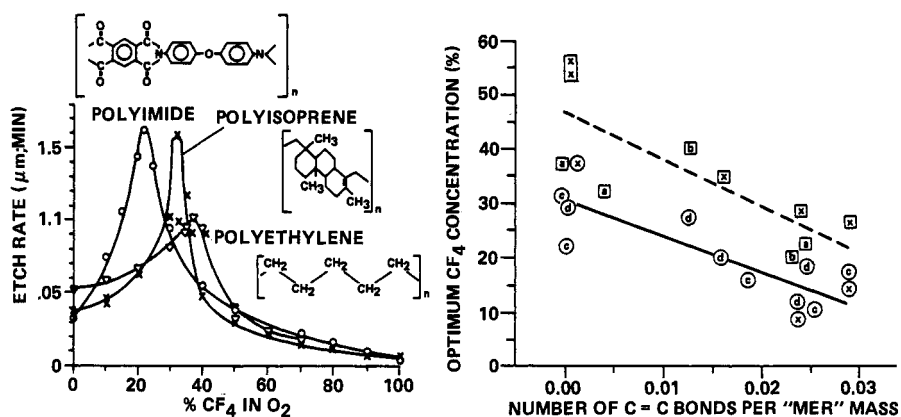


Fig. 3. (a) Etching rate versus gas composition for several polymers (after ref. 21). (b) Optimum  $\text{CF}_4$  concentration in the  $\text{O}_2/\text{CF}_4$  mixture versus degree of unsaturation for different polymers. Adapted from ref. 47. Data points labelled a, b, c, d, and x are from ref. 21, 50, 35, 47, and references contained in ref. 47, respectively. "□" denotes operation at 13.56 MHz and "○" denotes operation at 2.45 GHz.

### IONS AND PHOTONS

In the preceding sections, the participation of energetic species (ions, photons, excited metastables) on etching and modification processes has been largely ignored. Bond energies in polymers are in the range 2 to 5 eV. Golub and Wydeven (ref. 5) suggested that even the 5 eV collisional energy of LEO oxygen atoms with polyimide was sufficient to induce more facile polymer chain rupture. Certainly ions gaining 20 to several hundred eV of energy in traversing a plasma sheath can be expected to affect surface chemistry. The plasma is also a source of ultraviolet (UV) and vacuum ultraviolet (VUV) radiation, having energies greater than some polymer ionization potentials. Metastable species of noble gases can possess energies several times greater than typical polymer bond energies.

Gokan, et al. (ref. 49) observed that for  $\text{O}_2$  ion beam irradiation of various polymers, etching rates increased with ion accelerating voltages. The rate was found to be strongly dependent on the carbon content of the polymer and not so much on the structure or the strength of various bonds. For mixtures of  $\text{O}_2$  and  $\text{CF}_4$ , Occhiello, et al. (ref. 50) have shown that the increase in etching rate with bias voltage for plasma-polymerized polyethylene was relatively small and insensitive to variations in gas feed composition, suggesting an equal increase due to ions in the rate of all reactions, fluorination and oxidation, contributing to etching. Increases in etching rate with bias voltage for polystyrene and polycarbonate, being most pronounced around 50:50 mixtures of the feed gases, were proposed to indicate selective enhancement of reactions involving the aromatic ring. For poly (methyl methacrylate) (PMMA) and plasma-polymerized tetrafluoroethylene (PPTFE), enhancements varied with gas composition, possibly due to the ester functionality or fluorine content or the polymer, respectively.

For etching with mixtures of oxygen and fluorine-containing gases in the presence of ion bombardment, at least two investigations (ref. 51 & 52) have resulted in the observation of two etching rate maxima, one in the oxygen-rich regime and one in a fluorine-rich regime, and the appearance of  $\text{CF}_x$  etching products (ref. 51). It appears that ion bombardment induces more efficient removal of otherwise stable fluorocarbon products from polymer surfaces.

Helium, neon, and argon plasmas possess metastables with energies of 19.8, 16.6, and 11.5 eV, respectively. Schonhorn and Hansen (ref. 53) suggested that CASING (Crosslinking by Activated Species of Inert Gases) due to bombardment by  $\text{He}^+$  in radio-frequency plasmas resulted in increased bondability to polytetrafluoroethylene (PTFE). In addition, noble gas plasmas emit strongly in the VUV. Studies related to photon enhancement of polymer etching in plasmas are rare (ref. 54). However, much has been reported regarding the effect which radiation in the range from x-rays to UV has on polymer surfaces. Figure 4 shows the effect which treatment downstream from a helium microwave plasma has on DI water contact angle of PTFE films exposed simultaneously to photons and high energy metastables, and exposed to photons only. The latter condition was accomplished by use of a LiF crystal filter used to exclude helium, but pass VUV radiation with wavelength greater than 104 nm. For a photon

to cause modification, the polymer must absorb at the frequency of the photon (two photon interactions are far less likely, but possible at very high intensities). For most unsaturated polymers, modification is commonly obtained at wavelengths greater than 200 nm (energies less than 6 eV). However, absorption in pure PTFE and PE (saturated polymers) begins to fall off at wavelengths longer than 110 and 145 nm (11.3 and 8.6 eV), respectively (ref. 55 & 56). These energies are on the order of the first ionization potentials of the polymers (ref. 57 & 58). This restriction on minimum photon energy required for modification of these saturated polymers is qualitatively depicted in Fig. 5. Step-wise increments in short wavelength cut-off were obtained by changes in the crystal filter employed. Only for photons with energies on the order of the first ionization potentials of the polymers, and higher, were changes in contact angle observed.

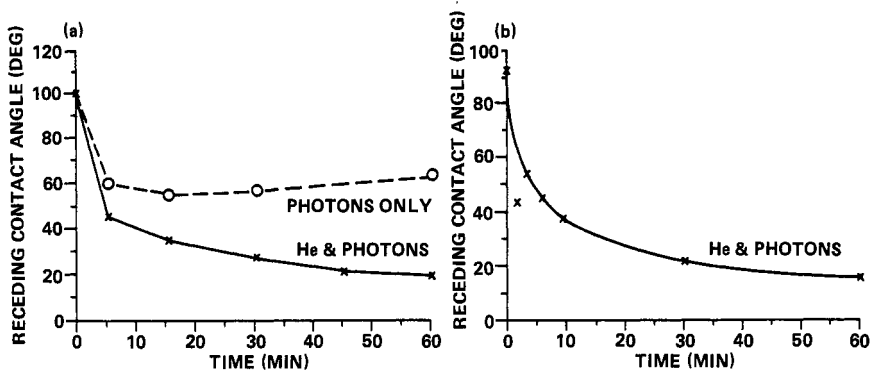


Fig. 4. Receding DI water contact angle versus treatment duration for films exposed downstream from He microwave plasmas; (a) PTFE, (b) PE.

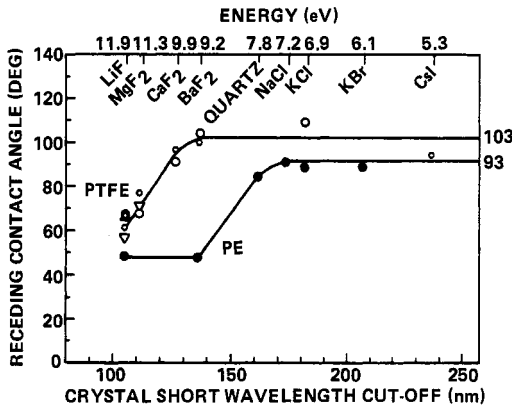


Fig. 5. Receding DI water contact angle for treated PTFE and PE films as a function of crystal short wavelength cut-off (photon energy). Exposure conditions were;  $\circ$  and  $\bullet$ , 60 minutes, 4mm thick crystal;  $\circ$  and  $\bullet$ , 15 minutes, 4 mm thick crystal;  $\Delta$  and  $\nabla$ , 60 minutes, 2 mm crystal; and  $\Delta$  and  $\nabla$ , 15 minutes, 2 mm thick crystal.

## CONCLUSIONS

An understanding of the effect of plasma reactor configuration and processing parameters on polymer etching rates and chemical modification allows for judicious selection of the polymer-plasma combination best suited to a specific application. Research in this area has accelerated in the past decade. However, the details of this highly convoluted problem are far from unravelled. Use of new surface analysis techniques, or old techniques applied to new problems, especially when used in a complementary fashion, will yield a far better understanding of the mechanisms and kinetics of these processes throughout the next decade.

## Acknowledgements

Collaboration with R.S. Horwath, F. Emmi, S.R. Cain, and L.J. Matienzo, IBM Corporation, and V. Vukanovic, G.A. Takacs, and R. Clark, Rochester Institute of Technology has been a pleasure and is acknowledged here.



## REFERENCES

1. S.J. Moss, in The Chemistry of the Semiconductor Industry, S.J. Moss and A. Ledwith, Eds., Blackie, Glasgow (1987), 391-412.
2. S.J. Moss, A.M. Jolly, and B.J. Tighe, Plasma Chem. and Plasma Process., 6(4), 401-416 (1986).
3. M.A. Hartney, D.W. Hess, and D.S. Soane, J. Vac. Sci. Technol. B 7(1), 1-13 (1989).
4. F.D. Egitto, V. Vukanovic, and G.N. Taylor, in Plasma Deposition of Polymer Films, R. d'Agostino, Ed., Academic Press, Boston, in press.
5. M.A. Golob, T. Wydeven, and R.D. Cormia, Polym. Communications, 29, 285-288 (1988).
6. S.M. Irving, Proc. Kodak Photoresist Seminar, 2, 26 (1968).
7. J.M. Moran and D. Maydan, J. Vac. Sci. Technol., 16(6), 1620-1624 (1979).
8. M. Hatzakis, J. Paraszczek, and J. Shaw, Proc. Int. Conf. on Microcircuit Engineering '81, A. Oosenberg, Ed., Lausanne, Switzerland, Sept. 28-30, 1981, 386-396.
9. G.N. Taylor, L.E. Stillwagon, and T.N.C. Venkatesan, J. Electrochem. Soc., 131, 1658-1663 (1984).
10. F. Coopmans and B. Roland, Solid State Technol., 30, 6, 93-99 Solid State Technol., 30, 6, 93-99 (1987).
11. R.H. Hansen, J.V. Pascale, T. De Benedictis, and P.M. Rentzepis, Journal of Polymer Science A, 3, 2205-2214 (1965).
12. J.R. Hall, C.A.L. Westerdahl, A.T. Devine, and M.J. Bodnar, J. Appl. Polym. Sci., 13, 2085-2096 (1969).
13. P. Spartacus, M. Goldman, and J. Amouroux, Proc. ISPC-8, K. Akashi and A. Kinbara, Eds., Tokyo, 1987, 1799-1804.
14. E.M. Liston and P.W. Rose, Proc. ISPC-7, C.J. Timmermans, Ed., Eindhoven, Neth., 1985, 219-224.
15. J.F. Battey, IEEE Transactions on Electron Devices, ED-24(2), 140-146 (1977).
16. J.M. Cook and B.W. Benson, J. Electrochem. Soc. 130(12), 2459-2464 (1983).
17. J.R. MacCallum and C.T. Rankin, Macromol. Chem. 175, 2477 (1974).
18. T. Wydeven, C.C. Johnson, M.A. Golub, M.S. Hsu and N.R. Lerner, in Plasma Polymerization, M. Shen and A. Bell, Eds., ACS Symposium Series, 108, American Chemical Society, Washington, D.C., 1979, 299-314.
19. H.J. Leary, Jr. and D.S. Campbell, in Photon, Electron, and Ion Probes of Polymer Structure and Properties, D.W. Wright, T.J. Fabish, and H.R. Thomas, Eds., ACS Symposium Series, American Chemical Society, 162, Washington, D.C., 1981, 419-433.
20. J.F. Rabek, in Singlet O<sub>2</sub>. Volume IV: Polymers and Biomolecules, A.A. Frimer, Ed., CRC Press, Inc, Boca Raton, Florida, 1985, 1-90.
21. S.R. Cain, F.D. Egitto and F. Emmi, J. Vac. Sci. Technol. A 5(4), 1578-1584 (1987).
22. R. Hoffmann and W.N. Lipscomb, J. Chem. Phys. 36, 2179 (1962). J. Chem. Phys. 36, 2179 (1962).
23. G.N. Taylor and T.M. Wolf, Polym. Eng. Sci., 20(16), 1087-1092, (1980).
24. S.J. Moss, A.M. Jolly, and B.J. Tighe, Proc. ISPC-6, M.I. Boulos and R.J. Munz, Eds., Montreal, 1983, 621-626.
25. F.D. Egitto, V. Vukanovic, F. Emmi, and R.S. Horwath, J. Vac. Sci. Technol. B 3, 893-904 (1985).
26. T. Wydeven, M.A. Golub, and N.R. Lerner, Proc. ISPC-8, K. Akashi and A. Kinbara, Eds., Tokyo, 1987, pp. 1368-1373.
27. M.A. Golub and T. Wydeven, Polymer Degradation and Stability, 22, 325-338 (1988).
28. L.J. Matienzo and F.D. Egitto, to be published.
29. A.D. Katnani, A. Knoll, and M.A. Mycek, J. Adhes. Sci. Technol., (1989), in print.
30. J.M. Cook, J.J. Hannon, and B.W. Benson, Proc. ISPC-6, M.I. Boulos and R.J. Munz, Eds., Montreal, 1983, 616-620.
31. J.E. Spencer, R.L. Jackson, and A. Hoff, in Proc. Symp. Plasma Process. PV87-6, G.S. Mathad, G.C. Schwartz, and R.A. Gottscho, Eds., Electrochemical Society, Pennington, NJ, 1987, pp. 186-200.
32. I.C. Plumb and K.R. Ryan, Plasma Chem. and Plasma Process., 6(3), 205-230 (1986).
33. M.J. Kushner, J. Appl. Phys. 53(4), 2939-2946 (1982). J. Appl. Phys. 53(4), 2939-2946 (1982).
34. E. Occhiello, M. Morra, F. Garbassi, and J. Bargon, Appl. Surface Sci., 36, 285-295 (1989).
35. V. Mugica, J.P. Kusior, E.A. Matuszak, R. Clark, G.A. Takacs, V. Vukanovic, F.D. Egitto, F. Emmi, and L.J. Matienzo, Proc. ISPC-9, R. d'Agostino, Ed., Pugnochiuso, Italy, 1989.
36. F. Egitto, V. Vukanovic, R. Horwath, and F. Emmi, Proc. ISPC-7, C.J. Timmermans, Ed., Eindhoven, Neth., 1985, 983-988.
37. M. Anand, R.E. Cohen, and R.F. Baddour, in Photon, Electron and Ion Probes of Polymer Structure and Properties, D.W. Dwight, T.J. Fabish, and H.R. Thomas, Eds., ACS Symposium Series, American Chemical Society, 162, Washington, D.C., 1981, 353-370.
38. J. Dedinas, M.M. Feldman, M.G. Mason, and L.J. Gerenser, Proc. First Annu. Int. Conf. Plasma Chem. Technol., H.V. Boenig, Ed., Technomic, Lancaster, Pennsylvania, 1983, 119-129.
39. J. Dedinas, M.M. Feldman, M.G. Mason, and L.J. Gerenser, private communication, presentation given at the Second Annual International Conference of Plasma Chemistry and Technology, San Diego, CA, 1984.

40. V. Vukanovic, G.A. Takacs, E. Matuszak, F.D. Egitto, F. Emmi, and R.S. Horwath, J. Vac. Sci. Technol., B 6(1), 66-71 (1988).
41. L.J. Matienzo, F. Emmi, F.D. Egitto, D.C. Van Hart, V. Vukanovic, and G.A. Takacs, J. Vac. Sci. Technol. A 6(3), 950-953 (1988).
42. V. Vukanovic, F.D. Egitto, F. Emmi, L.J. Matienzo, E. Matuszak, and G.A. Takacs, Proc. ISPC-8, K. Akashi and A. Kinbara, Eds., Tokyo, 1987, 933-938.
43. M. Strobel, S. Corn, C.S. Lyons, and G.A. Korba, J. Polym. Sci. Pol. Chem., 23, 1125-1135 (1985).
44. W.J. van Ooij and R.S. Michael, Proc. Symp. on Adhesion in Solids, Materials Research Society Spring Meeting, Reno, NV, 1988.
45. M. Kogoma and G. Turban, Plasma Chem. and Plasma Process., 6(4), 349-380, (1986).
46. M. Anand, R.E. Cohen, and R.F. Baddour, ACS Polymer Preprints 21(1), 139-140 (1980).
47. A.M. Wrobel, B. Lamontagne, and M.R. Wertheimer, Plasma Chem. and Plasma Process., 8(3), 315-329 (1988).
48. B. Robinson and S.A. Shivashankar, Proc. Symp. Plasma Process., PV 85-1, G.S. Mathad, G.C. Schwartz, and S. Smolinsky, Eds., Electrochemical Society, Pennington, NJ, 1985, 206-215.
49. H. Gokan, S. Esho, and Y. Ohnishi, J. Electrochem. Soc., 130, 143-146 (1983).
50. E. Occhiello, F. Garbassi, and J.W. Coburn, Proc. ISPC-8, K. Akashi and A. Kinbara, Eds., Tokyo, 1987, 947-952.
51. G. Turban and M. Rapeaux, J. Electrochem. Soc., 130(11), 2231-2236 (1983).
52. D.S. O'Grady, M.S. Thesis, Department of Material Science and Engineering, Lehigh University (1986).
53. H. Schonhorn and R.H. Hansen, J. Appl. Polym. Sci., 11, 1461-1474 (1967).
54. E.M. Liston, Proc. ISPC-7, C.J. Timmermans, Ed., Eindhoven, The Netherlands, 1985, pp. 513-517.
55. R.H. Partridge, J. Chem. Phys., 45, 1685-1690 (1966).
56. O.M. Sorokin and V.A. Blank, Zhurnal Prikladnoi Spektroskopii, 9(5), 827-829 (1968).
57. J. Delhalle, S. Delhalle, J.M. Andre, J.J. Pireaux, J. Riga, R. Caudano, and J.J. Verbist, J. Electron Spectroscopy and Rel. Phenom., 12, 293 (1977).
58. F.D. Egitto and L.J. Matienzo, to be published.