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## ABSTRACT

We have studied  $O_2/CF_4$  plasma etching of commercial polymers, particularly Kapton<sup>R</sup> polyimide, using a reactor in which the plasma can be excited by radiofrequency (rf, 13.56 MHz), or microwave power (mw, 2.45 GHz), or mixed frequency. For the case of rf plasma etching of polyimide, a marked effect of dc self-bias voltage  $V_s$  on the etch rate  $R$  has been observed;  $V_s$  is found to vary systematically with pressure and with  $CF_4$  concentration in the etch gas. In pure  $CF_4$  plasma we have found, for a series of polymers, that  $R$  depends on whether the polymers' structures incorporate oxygen or phenyl groups.

## 1. INTRODUCTION

Plasma etching has become an important technique for the removal of organic as well as inorganic materials used in various technological applications, particularly in microelectronics. In recent years, several authors /1-3/ including the present ones /4,5/ have investigated microwave (mw) plasma etching of polymers; in an earlier paper /5/ we compared 2.45 GHz mw and 13.56 MHz radiofrequency (rf) etching of polymers in  $O_2/CF_4$  gas mixtures, and we reported measurements of etch rates  $R$  and their dependence on molecular structure (particularly the degree of unsaturation) for a variety of commercial polymers. The present report complements the earlier one: we discuss here also mw and rf etch rates, particularly the effect of d.c. self-bias potential  $V_s$  in the capacitively coupled rf discharges. Finally, we examine the effect of polymer structure upon etching in pure  $CF_4$  plasma.

## 2. EXPERIMENTAL

The plasma apparatus, which can be used for mw, rf and mixed frequency plasma etching, has been described in detail elsewhere /4,5/. The stainless steel reactor chamber is rectangular (61.5 x 51 x 15 cm), with a 42 x 13.5 cm fused silica window through which microwave energy is applied from a 30 cm slow wave structure. In the rf operating mode, the same chamber is used to establish a capacitively coupled rf discharge between the electrically insulated sample holder (the powered electrode, connected to the 13.56 MHz rf source) and the grounded chamber wall. We have investigated two distinct rf etch modes, depending on the sample position: (i) connected to the chamber wall ("grounded electrode" mode) and (ii) placed upon the powered electrode. In the latter mode, plasma-chemical etching can be substantially modified by an additional (physical) effect, namely bombardment of the

sample surface by energetic ions. This, of course, results as positive ions from the plasma are accelerated through the plasma sheath, a dark region adjacent to the electrode surface /6/. The negative d.c. self-bias voltage  $V_s$  on the powered electrode is particularly pronounced when the electrode area ratio is large, as in the present case. We have measured  $V_s$  with the help of an inductance in series with an amperemeter and a voltage source. Many of the results reported here pertain to polyimide (DuPont Kapton "H"); other polymers are polyethylene terephthalate (Mylar<sup>R</sup>), polyamide (Nylon<sup>R</sup>), polypropylene, polystyrene, polymethyl methacrylate and polyacetal. The first four are available commercially in the form of foils; in the case of the latter three, we prepared films by melting commercial resin pellets in a hot press. The etch rate  $R$  (in  $\mu\text{m min}^{-1}$ ) was determined gravimetrically with an electronic microbalance and using known density values of the polymers. High purity oxygen and  $\text{CF}_4$  were used as etchant gases; all important experimental parameters (pressure, flow rates, etc) were electronically controlled and measured, as described earlier /4,5/.

### 3. RESULTS AND DISCUSSION

#### 3.1 RF Plasma Etching of Polyimide

Figure 1 shows a plot of etch rate  $R$  versus  $\text{CF}_4$  content in the  $\text{O}_2/\text{CF}_4$  mixture, for the case of rf etching of Kapton<sup>R</sup> in the "grounded electrode" mode.  $R$  is seen to rise with pressure in the range 0.1 to 2 Torr, and the maximum in  $R$  is seen to shift with rising pressure. A second maximum in  $R$  near 65%  $\text{CF}_4$  may be noted, but only in a limited pressure range ( $0.3 < p < 1.2$  Torr). It is not observed at all in microwave etching experiments. Turban et. al. /7,8/ have also reported this second maximum in their etch experiments of polyimide with  $\text{O}_2/\text{SF}_6$  mixtures. Its origin is not known at this time.

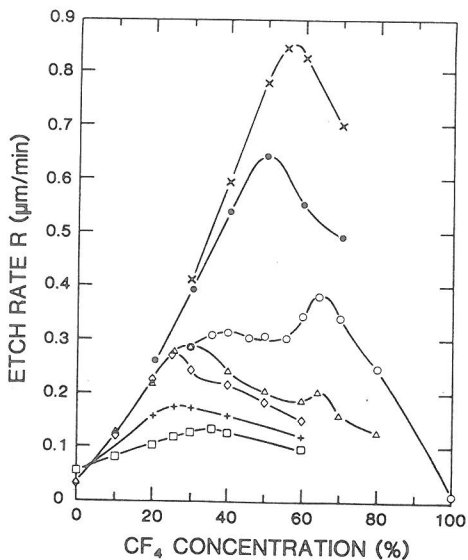


Fig. 1 Etch rate  $R$  of polyimide in rf plasma ("grounded electrode" mode,  $P = 100$  W) as a function of  $\text{CF}_4$  concentration in  $\text{O}_2/\text{CF}_4$ ;  $p$ (in Torr): □: 0.1; +: 0.2; ◇: 0.3; △: 0.5; ○: 0.8; ●: 1.2; x: 2.

When performing rf etch experiments in the "powered electrode" mode, very similar results as those shown in Fig. 1 are obtained, except at the lowest pressures and particularly for low  $\text{CF}_4$  concentrations. Figure 2 shows a plot of R for Kapton in pure  $\text{O}_2$  plasma, in the "grounded" and "powered" modes: whereas the former R values rise slightly with increasing pressure, the latter rise markedly with decreasing pressure. This is due to the additional effect of ion bombardment, which becomes more intense as  $V_s$  rises with decreasing pressure, as will be shown in the following section.

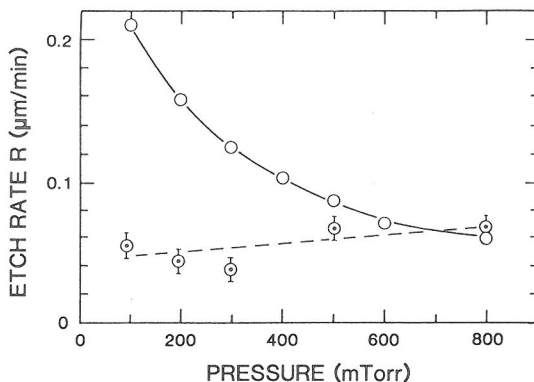


Fig. 2 Etch rate R of polyimide in pure  $\text{O}_2$  rf plasma versus pressure; the upper and lower curves correspond to the sample positioned on the "powered" and "grounded" electrodes, respectively.

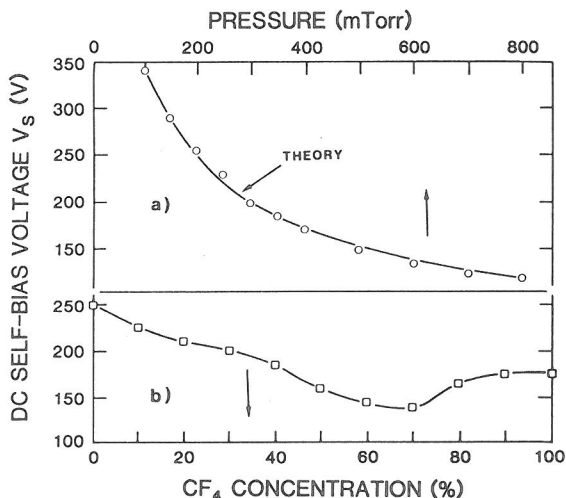


Fig. 3 (a) D.C. self-bias voltage  $V_s$  versus pressure in pure  $\text{O}_2$  rf plasma; the solid curve represents eq.(1) in the text; (b)  $V_s$  versus  $\text{CF}_4$  concentration in  $\text{O}_2/\text{CF}_4$  etch gas mixture ( $p = 0.2$  Torr,  $P = 100$  W).

### 3.2 Measurements of $V_s$

Figures 3(a) and (b) show  $V_s$  measurements as a function of pressure for pure  $O_2$ , and as a function of  $CF_4$  concentration at constant pressure (200 mTorr), respectively. By a simple calculation of the current density in the rf plasma, as have done Catherine and Couderc /9/, one can show that

$$V_s \propto (P/p)^{1/2} \quad (1)$$

where  $P$  and  $p$  are the power and pressure, respectively. When the plasma power is kept constant, as in the present experiments, one may expect  $V_s$  to vary inversely as  $p^{1/2}$ . The solid curve in Fig. 3(a), which represents this function, is seen to fit the experimental data for pure  $O_2$  plasma rather well. The rise in  $R$  with decreasing pressure (Fig. 2), attributed to the physical effect of ion bombardment, thus appears well substantiated by the data in Fig. 3(a).

Regarding the dependence of  $V_s$  on gas composition, Fig. 3(b) reveals a minimum in  $V_s$  near 70%  $CF_4$ . The addition of  $CF_4$  to an oxygen plasma affects the yield of O atoms and ions, as well as the electron energy distribution function EEDF /10/. Walkup et. al. /11/ have also observed drops in  $V_s$  as they added  $CF_4$  to  $O_2$  plasma, and Egitto et. al. /12/ have obtained a curve similar to Fig. 3(b) for the peak-to-peak rf voltage applied at the powered electrode. According to the above-cited model of Catherine and Couderc /9/,  $V_s$  should increase if the electronic conductivity of the plasma increases. Now, the ionization thresholds for  $CF_4$  and  $O_2$  are 15.4 and 12.2 eV, respectively; if one assumes an essentially invariant EEDF,  $O_2$  plasma should be more conductive than  $CF_4$  plasma, and hence  $(V_s)_{O_2} > (V_s)_{CF_4}$  as found in Fig.

3(b). The observed complex behaviour of  $V_s$  as a function of  $CF_4$  concentration is presumably due to variations in electron density and EEDF with varying gas composition.

### 3.3 MW/RF Comparison and Effect of Polymer Structure

We noted, in connection with Fig. 1, a systematic shift of the "optimum"  $CF_4$  concentration (that corresponding to the maximum value of  $R$ ) with pressure. In Fig. 4 we plot this value,  $(CF_4)_{opt}$  versus pressure for the two rf modes, and for mw plasma. In all three cases  $(CF_4)_{opt}$  displays a minimum near 300 mTorr, and at any given pressure the mw values are lower than the corresponding rf data by a factor ranging from about 1.3 to 1.5.

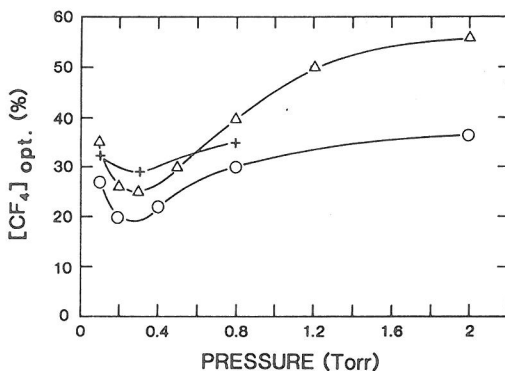




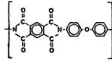
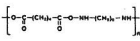
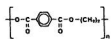


Fig. 4 "Optimum"  $CF_4$  concentration (see text) for polyimide etching in rf plasma ( $\Delta$ : "grounded", +: "powered" electrode modes), and mw plasma ( $\circ$ );  $P_{rf} = 100$  W;  $P_{mw} = 350$  W.

Although rf and mw plasmas generally display visible differences, for example in the location and volume of the glow region, it is nevertheless possible to compare R values under otherwise identical experimental parameters. When this is done,  $R_{\max}$  for mw under "optimum" conditions is a factor of about 3 greater than its rf counterpart. This may be attributed to differences in the EEDF between rf and mw, as first suggested by Wertheimer and Moisan /13/.

Sauvé et. al. /3/ have reported a systematic study of polyimide etching in high frequency surface wave plasmas, ranging from  $\omega = 27$  MHz to 2.45 GHz. They show "three dimensional" plots of R versus  $[CF_4]$  and P at several fixed frequencies in the above range. The highest R/P value was observed near 50 MHz, and  $R_{\max}$  and  $(CF_4)_{\text{opt}}$  were found to shift with  $\omega$  in a complex manner, as indicated also by the present 13.56 MHz and 2.45 GHz data. These observations all bear witness to the great complexity of this plasma chemical reaction system; much additional information, for example from plasma diagnostics and modelling, is required if one is to gain insight into the detailed reaction mechanisms and their dependence on experimental parameters.

In an earlier paper /5/ we reported the ratio between rf and mw values of  $(CF_4)_{\text{opt}}$  (see above) to be roughly constant ( $\sim 1.7$ ) for a series of nine commercial polymers of widely differing compositions, structures and "degrees of unsaturation" (number of C=C double bonds per repeat unit). In Table I we show the results from mw plasma etch experiments in pure  $CF_4$  ( $P = 220$  W,  $p = 300$  mTorr) for the case of seven different polymers; also shown is the structure of the repeat unit, and its oxygen content (number of O atoms per molecular mass of the "mer", or repeat unit). From this table, the etch rate under the given set of conditions appears directly related to the polymers' oxygen contents. This is not unexpected, for as the oxygen is liberated from the polymer it can partake in the gas phase etch reaction.

Table 1  $CF_4$  Microwave Plasma Etching of Polymers

POLYMER	STRUCTURE	$\left[ \frac{[O]}{M} \right]^*$	R ( $\mu\text{m/min}$ )
Polystyrene		0	0.02
Polypropylene		0	0.08
Polyimide		0.0128	0.10
Nylon		0.0155	0.12
Mylar		0.022	0.14
PMMA		0.020	0.21
Polyacetal		0.033	1.35

\*  $[O]$  = number of O atoms per repeat unit; M = molecular weight of the repeat unit

This may be considered as a counterpart to the "catalytic effect", first suggested by Taylor and Wolf /14/, of halogens such as fluorine incorporated in the polymer structure, when the polymer is exposed to a pure oxygen plasma.

Another apparent correlation emerging from Table 1 involves aromaticity in the structures: Aromatic polymers are known to be relatively resistant towards oxygen plasma etching. This also appears to be the case in  $CF_4$  plasma, if we compare for example polystyrene and polypropylene. This agrees with Pederson's /15/ results on five different polymers etched in  $CF_4$  rf plasma.

#### 4. CONCLUSIONS

The present report illustrates, once again, that excitation frequency is a major parameter in plasma chemistry. Plasma etching of polymers presents a particularly complex chemistry as certain constituents of the polymer structure, when volatilized even in small concentrations, can profoundly modify the plasma characteristics. Understanding all the complex features observed here will call for important efforts in diagnostics and modelling.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] J. Paraszczak, M. Hatzakis, E. Babich, J. Shaw, E. Arthur, B. Grenon, and M. DePaul, *Microelectronic Eng.*, **3**, 397 (1985).
- [2] V. Vukanovic, G.A. Takacs, E.A. Matuszak, F.D. Egitto, F. Emmi, and R.S. Horwath, *J. Vac. Sci. Technol.*, **B6**, 66 (1988).
- [3] G. Sauvé, M. Moisan, J. Paraszczak, and J. Heidenreich, *Appl. Phys. Lett.*, **53**, 470 (1988).
- [4] B. Lamontagne, A.M. Wrobel, G. Jalbert, and M.R. Wertheimer, *J. Phys. D: Appl. Phys.*, **20**, 844 (1987).
- [5] A. M. Wrobel, B. Lamontagne, and M.R. Wertheimer, *Plasma Chem. Plasma Process.*, **8**, 315 (1988).
- [6] B. Chapman, "Glow Discharge Processes", Wiley, New York (1980).
- [7] G. Turban and M. Rapeaux, *J. Electrochem. Soc.*, **130**, 2231 (1983).
- [8] M. Kogoma and G. Turban, *Plasma Chem. Plasma Process.*, **6**, 349 (1986).
- [9] Y. Catherine and P. Couderc, *Thin Solid Films*, **144**, 265 (1986).
- [10] M.J. Kushner, *J. Appl. Phys.*, **53**, 2939 (1982).
- [11] R.E. Walkup, K.L. Saenger, and G.S. Selwyn, *J. Chem. Phys.*, **84**, 2668 (1986).
- [12] F.D. Egitto, F. Emmi, R.S. Horwath, and V. Vukanovic, *J. Vac. Sci. Technol.*, **B3**, 893 (1985).
- [13] M.R. Wertheimer and M. Moisan, *J. Vac. Sci. Technol.*, **A3**, 2643 (1985).
- [14] G.N. Taylor and T.M. Wolf, *Polym. Eng. and Sci.*, **20**, 1087 (1980).
- [15] L.A. Pederson, *J. Electrochem. Soc.*, **129**, 205 (1982).