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LARGE AREA MICROWAVE PLASMA ETCHING OF POLYMERS

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ABSTRACT

We have investigated O_2/CF_4 plasma etching of five commercial polymers: polyimide (Kapton "H"[R]), polyamide (Nylon 66), polyester (Mylar[R]), polycarbonate (Lexan[R]), and cured epoxy resin (DER[R] 566-A80, FR-4). A new large area microwave plasma apparatus has been used in this work. The effect of operating parameters such as pressure, etchant gas composition, and sample temperature upon etch kinetics have been examined. We have observed sharp maxima in the etch rate versus pressure and versus CF_4 concentration. The temperature dependence shows that etching is a thermally activated process in all cases. The associated activation energies evaluated from the Arrhenius plots fall in the range 0.04-0.2 eV, in agreement with data in the literature.

1. INTRODUCTION

Plasma etching has become an important technique for the removal of organic as well as inorganic materials used in various technologies, particularly in microelectronics. This technique, also known as dry etching, (in contrast to wet-chemical etching), offers numerous advantages including high etch rate and the ease of controlling both etch rate and directionality by varying certain plasma operating parameters (1).

Among the various power source frequencies used for the etching process, microwave (MW) excitation appears to be particularly effective due to the relatively higher population of energetic electrons, compared to the electron energy distribution function (EEDF) that for lower frequency excitation (2). In a previous paper (3) we presented results on O_2/CF_4 plasma etching of polyimide film using a new large area microwave plasma apparatus (Polyplasma "LMP 83-3") which yields etch uniformity of better than ±7% over a 700 cm^2 sample area. The present study is devoted to optimizing the etch process for five commercial polymers using the LMP 83-3 apparatus: polyimide (Kapton "H"), polyamide (Nylon 66), polyester (Mylar), polycarbonate (Lexan), and cured epoxy resin (DER 566-A80, FR-4). The optimum pressures, etchant gas compositions, as well as maximum etch rate and thermal activation energy values have been evaluated for each polymer under optimized conditions, and they are reported here.

2. EXPERIMENTAL

Although the "LMP 83-3" microwave plasma etch apparatus used here has already been described elsewhere (3), it is useful to recall some of its principal features: It comprises a 61.5 x 51 x 15 cm stainless steel reactor chamber into which 2.45 GHz microwave power is applied from a 30 cm-long strapped bar slow wave structure (4), through a rectangular (42 x 13.5 cm) fused silica window; in some instances the effective width was reduced to 7.5 cm using thin metal screens, in order to

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minimize the effect of dielectric heating by the microwave field (3). Inside the chamber the 32 cm diameter stainless steel sample holder is coupled to a mechanism which can provide it with simultaneous rotational and translational motion during etching, a process which is designed to maximize etch uniformity over the entire sample surface. Infrared heating elements located on either side of the microwave window are used to uniformly heat the sample holder to temperatures in the range $25°C < T \leq 300°C$, if required. Microwave power up to 1 kW is supplied from a continuously variable magnetron-based unit. The chamber is evacuated using a two-stage rotary vane pump, filled with fluorinated (Fomblin) pump oil. Gas pressure, and O_2 and CF_4 flow rates are controlled using a capacitive (MKS Baratron) pressure gauge and throttle valve and electronic mass flow controllers (Vacuum General), respectively. Sample temperature during etching is monitored using a surface-mounted chromel-alumel thermocouple, while power absorbed by the plasma (P) is measured from the difference between incident, and transmitted and reflected power values.

The polymer films used in the present study are identified in Table 1. The epoxy resin was obtained in the form of a "prepreg" composite with fibre glass fabric which was cured at 177°C using dicyanodiamide as the curing agent. Circular film samples, 9 cm in diameter, were mounted centrally on the substrate holder which was rotated at 6 rpm in all experiments. In order to evaluate the temperature dependence of etch kinetics, combined rotation and translation (40 cm/min) was applied to the sample holder so as to obtain uniform heating. The etch rate R (µm/min) was determined gravimetrically from weight loss of the sample using the density values shown in Table 1. In all cases high purity oxygen and carbon tetrafluoride, supplied by Union Carbide were used as etchant gases.

3. RESULTS AND DISCUSSION

The effect of O_2/CF_4 pressure on the etch rate of the various polymer films is presented in Fig. 1. We note that the curves for Kapton "H", Nylon 66, and Mylar were evaluated with the microwave window partially screened to 7.5 cm width; the lower observed etch rates in these cases result from the shorter residence time in the glow discharge. A general feature of the curves in Fig. 1 is the presence of a sharp maximum in etch rate which identifies the optimum pressure value, $p_{opt.}$, characteristic of each of the polymers investigated. The p_{opt} values are listed in Table 2.

The appearance of a maximum in the R vs. p curves bears witness to a complex etch mechanism, and it appears to result from a variation of the concentration of etch precursors, primarily oxygen and fluorine atoms. Dzioba et. al. (5) have used optical emission spectroscopy as a diagnostic tool for pure O_2 microwave plasma etching of photoresist; they observed a maximum in the emission intensity of atomic oxygen (OI 486 nm) at a pressure near 0.1 Torr and also found that this nearly coincided with their etch rate maximum. The observed rise in R to its maximum for $p \leq p_{opt}$ noted in Fig.1 can therefore be attributed to a rise in concentration of etch precursors, particularly atomic oxygen. The drop in R beyond p_{opt} evidently results from a decrease in their concentration; this is probably primarily due to increased recombination of O atoms and to collisional quenching of other excited species. It is noteworthy, however, that a pressure increase can also modify the EEDF in such a way as to decrease the population of energetic electrons (2), thus decreasing the rate of generation of O and F atoms. The fact that all the maxima in Fig 1 fall within the narrow pressure range $0.14 \leq p \leq 0.25$ Torr (in spite of the very different structures of the polymers studied - see also below), we feel, supports the view that O atom concentration is the principal factor governing R: note that R_{max} for Epoxy,

Nylon and Mylar occurs at precisely the same value of p_{opt} (= 0.14 Torr).

Fig. 2 shows the etch rate of the polymers studied, as a function of CF_4 concentration, $[CF_4]$, in the gas feed. The curves for Lexan and Epoxy were evaluated with the unscreened microwave window, while the remaining curves were obtained with its width reduced from 13.5 to 7.5 cm. In all cases R rises sharply with increasing $[CF_4]$ to a maximum value at $[CF_4]_{opt}$, and these values are presented in Table 2. The curves presented here are consistent with optical emission spectroscopic data on MW (6) and RF (7) plasma etching of polyimide and of epoxy resin (8), which revealed that the emission intensity of atomic oxygen increases dramatically with the addition of CF_4, and that the highest etch rate occurs at an optimum value of the [O]/[F] emission intensity ratio (6,7,8).

It is now generally accepted that the role played by CF_4 (or other fluorinated compound such as SF_6) is the following: fluorine atoms produced by dissociation of CF_4 can abstract hydrogen atoms from the polymer, thus creating radical sites on the surface which readily undergo reactions with oxygen atoms to form volatile products (CO, CO_2, COF_2) (9,10). This explains the increase in R to a maximum value for $[CF_4] \lesssim [CF_4]_{opt}$. as observed in Fig. 2. For $[CF_4] > [CF_4]_{opt}$. the polymer surface becomes passivated by the formation of chemically stable fluorocarbon groups which strongly impede the etching process. The XPS data of Egitto et. al. showed clearly that a pronounced fluorination of a polyimide surface occurs at $[CF_4] > 20\%$ the value corresponding to their etch maximum; - CF_2 - groups, in particular, were found to predominate in the surface structure. Recent work by Kogoma and Turban (10), also on plasma etching of polyimide, revealed deposition on the etched surface of a material with elemental composition $C_n H_m O_x F_y$ (n=1, x=1.5, $y \lesssim 3.3$), a coating which appears to obstruct the etching reactions. These mechanisms appear to account for the decrease in etch rate at $[CF_4] > [CF_4]_{opt}$ observed in Fig 2. The fact that $[CF_4]_{opt}$ varies, depending upon the particular polymer structure (see Table 2), has been explained by Cain et. al. (11) in terms of molecular orbital theory which predicts a decrease in $[CF_4]_{opt}$ with increasing degree of unsaturation in the macromolecule. This finding agrees reasonably well with both their own as well as our data; the latter clearly show $[CF_4]_{opt}$ of polymers containing aromatic rings (Kapton "H", Mylar, Lexan, Epoxy) to be lower than that of the saturated polymer-Nylon 66.

Fig. 3 presents the etch characteristics of the present polymers, evaluated under optimum pressure and CF_4 concentration, namely the values given in Table 2. In all cases, etch depth is seen to increase linearly with etch duration; optimum etch rates for P = 230 W (the slopes of these plots) are also listed in Table 2. It is interesting to note that these R values, from ~ 1.1 µm/min for Mylar to ~ 1.4 µm/min for Lexan, do not differ very substantially.

The effect of polymer surface temperature on the etch rate is illustrated in Fig. 4 in the form of Arrhenius plots (ℓn R vs. reciprocal absolute temperature). The plots pertain optimum pressure and CF_4 concentration conditions listed in Table 2, where the apparent activation energy (E_a) values, obtained from the slopes by least square fits, are also shown. In the case of polyimide (Kapton "H"), for example, the present value of 0.21 eV agrees with the results of Paraszczak et. al. (6), who found E_a to increase from 0.05 eV for pure O_2 plasma to 0.27 eV for O_2/CF_4 plasma with $[CF_4] \geq 20\%$. For downstream etching of the same polymer in a microwave-generated ternary gas ($O_2/Ar/CF_4$) plasma with 20% CF_4, Vukanovic et. al. (12) found $E_a = 0.14 \pm 0.03$ eV.

In view of the aforementioned variation of E_a with etchant gas composition, it is difficult to compare E_a values from Table 2, which are evaluated on the basis of the different optimum etch conditions.

Nevertheless, considering linear polymers, it is possible to discern a correlation between E_a values and the types of heteroatoms present in the polymer chain: polymers containing nitrogen atoms (Kapton "H", Nylon 66) exhibit substantially higher E_a values than those containing only oxygen (Mylar, Lexan). Moreover, the expected correlation between high etch rate and low activation energy is observed in the case of Lexan; this polymer's high susceptibility to plasma etching is presumably due to the presence of carbonate groups which readily undergo chain-breaking reactions. Finally, considering Epoxy, the exceptionally low E_a value found for this polymer presumably results from the presence of bromine substituents in the aromatic ring (see Table 1) which, when volatilized, may play a catalytic role similar to that of fluoring in the etch process. The active sites for etching reactions may be accompanied here by elimination of HBr. A similar catalytic effect has been observed in plasma polymerization, where the presence of halogen atom in the monomer molecule markedly enhances the generation of polymerization precursors (13).

4. CONCLUSIONS

The present study of O_2/CF_4 microwave plasma etch kinetics of various commercial polymers has shown that optimum pressure and etchant gas composition depend strongly on polymer structure. Among the materials investigated, polycarbonate-Lexan was found to be that most susceptible to plasma etching, but optimum etch rates were found to vary by only about 30% between it and the least susceptible (polyester-Mylar). There appears to exist a correlation between polymer structure and activation energy for etching: the presence of nitrogen atoms in the polymer chain raises E_a, whereas materials with oxygen atoms have a low E_a value. Bromine in the structure of Epoxy resin appears to play a catalytic role in etching which leads to an extremely low E_a value.

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Table 1. Characteristics of the Polymer Films used for Etching

POLYMER (PRODUCER)	STRUCTURAL FORMULA	DENSITY (g/cm^3)	INITIAL FILM THICKNESS (μm)
POLYIMIDE-KAPTON "H"® (DU PONT)	$-[N(C(=O))_2C_6H_2(C(=O))_2N-C_6H_4-O-C_6H_4]_n-$	1.42	50
POLYAMIDE-NYLON 66 (DU PONT)	$-[O-C(=O)-(CH_2)_4-C(=O)-O-NH-(CH_2)_6-NH]_n-$	1.13	26
POLYESTER-MYLAR ® (DU PONT)	$-[O-C(=O)-C_6H_4-C(=O)-O-(CH_2)_2]_n-$	1.40	14
POLYCARBONATE-LEXAN ® (GENERAL ELECTRIC)	$-[C_6H_4-C(CH_3)_2-C_6H_4-O-C(=O)-O]_n-$	1.20	26
EPOXY RESIN-DER® 566-A80, FR-4 (DOW CHEMICAL)	$[>N-CH_2CH(N<)CH_2-[O-C_6H_2Br_2-C(CH_3)_2-C_6H_2Br_2-OCH_2-CH(-N<)-CH_2O-C_6H_2Br_2-C(CH_3)_2-C_6H_2Br_2]_m-OCH_2CH(N<)CH_2-N<]_n$	1.36	127

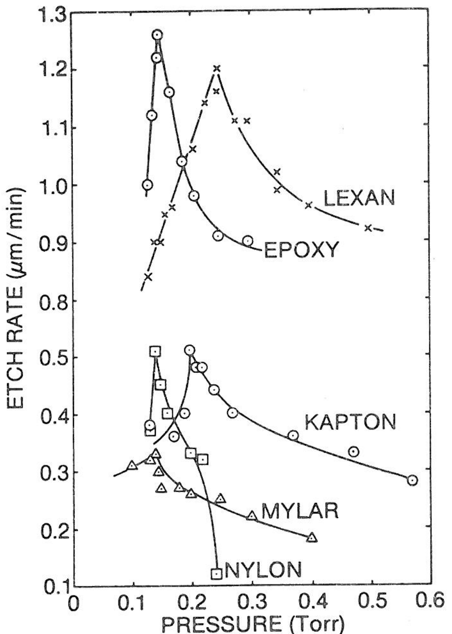

Fig. 1. Etch rate of the polymer films as a function of O_2/CF_4 pressure. Etch conditions: Kapton "H", $[CF_4]$ = 11%, P = 370 W; Nylon 66, $[CF_4]$ = 11%, P = 210 W; Mylar, $[CF_4]$ = 11%, P = 220 W; Lexan, $[CF_4]$ = 11%, P = 220 W; Epoxy, $[CF_4]$ = 20%, P = 260 W; O_2/CF_4 flow rate = 70 sccm in all cases.

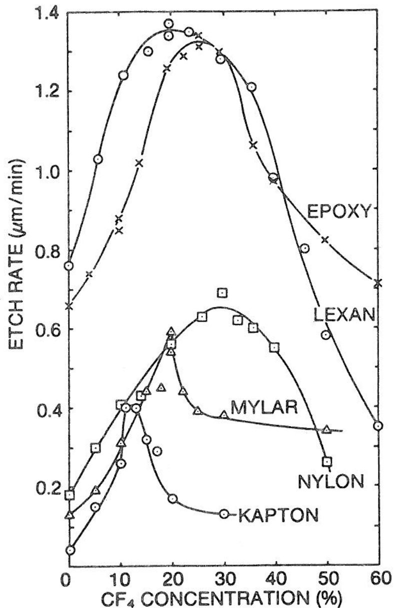

Fig. 2. Etch rate of the polymer films as a function of CF_4 concentration. Etch conditions: Kapton "H", p = 0.27 Torr, P = 400 W; Nylon 66, p = Torr, P = 240 W; Mylar, p = 0.14 Torr, P = 210 W; Lexan, p = 0.25 Torr, P = 230 W; Epoxy, p = 0.15 Torr, P = 260 W; O_2/CF_4 flow rate = 70 sccm in all cases.

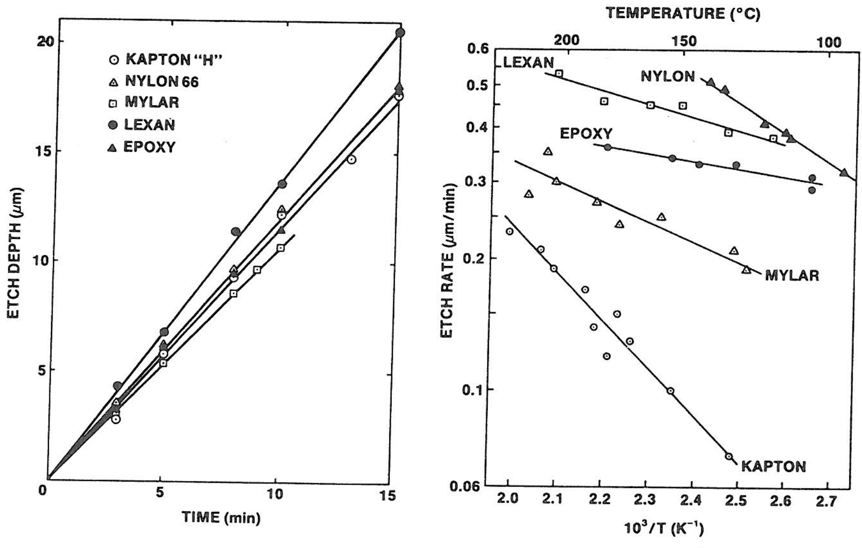

Fig. 3. Etch characteristics evaluated under optimized pressure and CF_4 concentration conditions; O_2/CF_4 flow rate = 70 sccm, P = 230 W.

Fig. 4. Etch rate as a function of reciprocal temperature of the polymer films. Etch conditions: O_2/CF_4 flow rate = 70 sccm, $p_{opt.}$ and $[CF_4]_{opt.}$ values as in Table 2; Kapton "H", P = 170 W; Nylon 66, P = 160 W; Mylar, P = 210 W; Lexan, P = 160 W; Epoxy, P = 170 W.

Table 2. Summary of the Etch Kinetics Study

Polymer	$P_{opt.}$ (Torr)	$[CF_4]_{opt.}$ (%)	R* (μm/min)	Ea (eV)
Kapton "H"	0.20	12	1.19 ± 0.03	0.21 ± 0.02
Nylon 66	0.14	30	1.21 ± 0.02	0.14 ± 0.01
Mylar	0.14	20	1.09 ± 0.01	0.08 ± 0.01
Lexan	0.25	20	1.37 ± 0.02	0.06 ± 0.01
Epoxy	0.15	26	1.21 ± 0.03	0.04 ± 0.01

*) P = 230 W.