

# Reactive Ion Etching of Selected Polymers in O<sub>2</sub> and in CF<sub>4</sub>/O<sub>2</sub>

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## SYNOPSIS

A series of 17 polymers was etched in the reactive ion-etching (RIE) mode. The etch rates were monitored using a laser interferometer. The gases used were oxygen alone and a mixture of carbon tetrafluoride with oxygen (8% O<sub>2</sub>). The polymers fell into three groups: the aromatics (polystyrene and derivatives), the aliphatics (methacrylates and vinyl acetate), and the cellulose (methyl ether and nitrate). In oxygen with a power density of 0.25 W/cm<sup>2</sup>, the etch rates for the three groups fell in the range of 200–300 nm/min, 350–450 nm/min, and 500–850 nm/min, respectively. The etch rates were also measured at a power density of 0.50 W/cm<sup>2</sup>. The etch rates at the higher-power density were about 75–80% higher than those at the lower-power density. The etch rate in the fluoride mixture was about half that in the oxygen, all other parameters being the same. Plasticizers that lower the glass transition temperature of polymers based on vinyl chloride, methyl methacrylate, or styrene do not change the etch rate of the polymers very much. There is a slight increase in the rate for polystyrene and a slight decrease in the rate for poly(methyl methacrylate). All the effects of composition on etching rate can be correlated to a first approximation with the molar fractions of carbon and oxygen in the resist. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The submicron geometries required as integrated circuit features shrink often demand the use of highly anisotropic etching processes, i.e., ion-assisted or reactive ion etching (RIE). A successful pattern transfer in the lithographic process depends on having a polymer "stencil" that will resist aggressive plasma-etching environments.

The complex nature of the plasma/surface interactions makes it difficult to achieve a complete understanding of the degradative mechanisms for polymer resists under "typical" plasma or RIE conditions. Much can be learned by observing the etching characteristics of a variety of chemical structures.

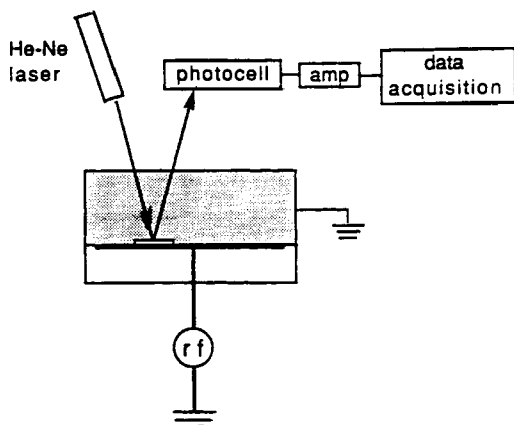
Some common gases used in RIE are oxygen and a mixture of carbon tetrafluoride with oxygen (8% O<sub>2</sub> being a usual concentration).<sup>1</sup> Oxygen plasmas

have been used for a long time for resist stripping. In recent years, however, O<sub>2</sub> RIE has also become an important part of some multilayer resist systems as well as of dry-developing schemes based on silyl-derivatization. The fluoride gases have been used for etching silicon and silicon oxide.

## EXPERIMENTAL

The parallel-plate system (Fig. 1) has a cathode (negative potential) housed in a chamber with a bulk plasma maintained at a small positive potential.<sup>2</sup> The top lid has a quartz window through which a 2 mW He—Ne laser beam passes and is reflected from the surface of the wafer under test. The oscillations of the reflected light intensity are used to estimate the actual etch rate. Also included in the apparatus are a variable orifice to control the chamber pressure (in the range of 1–100 mTorr), gas flow valves, nitrogen backfill for the chamber, and the usual diffusion and roughing pumps. A radio-frequency (13.56 MHz) generator (HFS 2000 D, Plasma-

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**Figure 1** Sketch of laser interferometer.

Therm) and an impedance matching network (AMN-2000, Plasma-Therm) power the cathode, which is kept at 25°C by circulating a water-glycol mixture.

Four conditions were employed in exploring the effects of structure on etch rate. Two gases ( $O_2$  and  $CF_4/O_2$  8%) were used at two power densities: 0.25 and 0.50 W/cm<sup>2</sup>. In all cases, the chamber pressure was  $40 \pm 5$  mTorr and the gas flow rate was 20 standard cm<sup>3</sup>/min.

Polymer films were spun on 3 in.-diameter silicon wafers from 5–10% solutions in appropriate solvents. All wafers were baked at 160°C for 1 hr. The polymers used were either commercially available materials (Tables I and II) or made by us.

To convert the reflected light patterns into etching rates, the index of refraction of the films had to be known. Where they were not already known from previous work, they were measured on the wafers ellipsometrically (Table I).

## RESULTS AND DISCUSSION

### RIE in Oxygen at Low (0.25 W/cm<sup>2</sup>) Power Density

The polymers tested fall into three groups (Table I): The aromatics (polystyrene and derivatives) etch at rates of 200–300 nm/min. The aliphatic polymers (based on methacrylates and vinyl acetate) etch more rapidly: 350–450 nm/min. The cellulose-based polymers etch more rapidly still: 500–850 nm/min.

There have been a number of studies in which a variety of chemical structures have been classified as to etching rate.<sup>3–13</sup> Most workers agree that poly-

mers containing aromatic rings resist etching more than do aliphatic polymers. Some<sup>2</sup> have found an almost linear relationship between etching rate in oxygen and aromatic content with poly-(methyl methacrylate) (PMMA) and poly( $\alpha$ -methyl styrene) at the extremes. Of course, certain other elements, notably silicon and tin among others, can enhance etch resistance greatly<sup>2</sup> by forming refractory oxides. In the present work, we consider only polymers that do not contain such elements.

Gokan et al.<sup>10,11</sup> proposed a more general criterion for estimating etch behavior. They reasoned that etch rate, regardless of the gas used, is dominated by sputtering. If carbon is the major factor in controlling the sputtering yield, the molar fraction of carbon in the polymer repeat unit might be the only parameter needed to correlate with etch rate. However, they found that a much better fit was obtained when the molar fraction of oxygen was subtracted from that of carbon. The dimensionless group that results is

$$N_T/(N_c - N_o) \quad (1)$$

where  $N_T$  is the total number of atoms in the repeat unit;  $N_c$ , the number of carbon atoms; and  $N_o$ , the number of oxygen atoms. For oxygen-ion-beam etching of a group of polymers, Gokan's correlation is approximately

$$= 50 + 80[N_T/(N_c - N_o)] \quad (2)$$

It is obvious that in a polymer where equal numbers of carbon and oxygen atoms are present such as polyoxymethylene the predicted etch rate would be infinite. One of the polymers in the present study, cellulose nitrate, has more oxygen than carbon atoms, giving a negative value for eq. (1). A semilog plot of etch rate vs. composition expressed as  $C_G$  is more satisfactory (Fig. 2, line B) where the ratio proposed by Gokan now is

$$C_G = (N_c - N_o)/N_T \quad (3)$$

The discontinuity where the number of carbon atoms equals or exceeds the number of oxygen atoms is avoided. All the 17 points for the rate fit within  $\pm 30\%$  of the line corresponding to

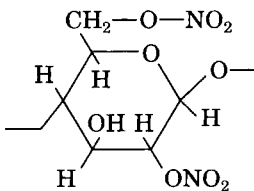
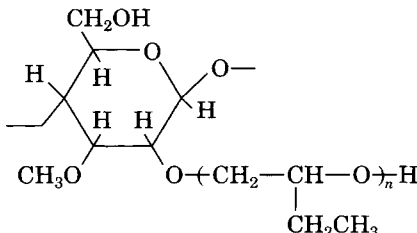
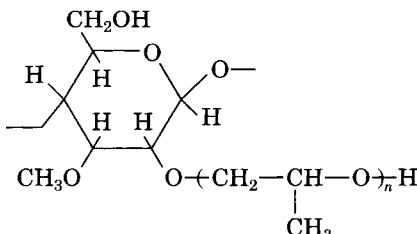
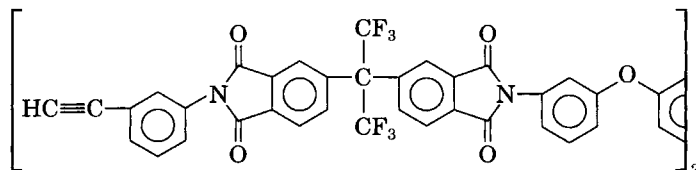
$$\log [\text{Rate (nm/min)}/640] = -1.10C_G \quad (4)$$

Table I Polymers (Etched in Oxygen at 0.25 W/cm<sup>2</sup>)

Abbrev.	Composition	Refractive Index	Etch Rate (nm/min)	CG	Trade Name	Commercial Source	Spinning Solvent
CEN	Cellulose nitrate	1.50	835	-0.15	—	—	POMA*
MHB	Methoxycellulose (with butoxy)	1.470	530	0.17	Methocel™ HB	Dow	Water
MHG	Methoxycellulose (with propoxy)	1.502	470	0.17	Methocel™ HG	Dow	Water
PVAc	Poly(vinyl acetate)	1.467	375	0.17	—	—	Cyclohexanone
AN	Copolymer of vinyl methyl ether and maleic anhydride	1.47	355	0.19	Gantrez AN™	GAF	NMP*
PMMA	Poly(methyl methacrylate)	1.489	415	0.20	—	—	Chlorobenzene
PEMA	Poly(ethyl methacrylate)	1.485	410	0.22	—	—	Chlorobenzene
PBMA	Poly( <i>n</i> -butyl methacrylate)	1.483	390	0.25	—	—	Chlorobenzene
VMC	Terpolymer of vinyl chloride (86%), vinyl acetate (13%), maleic anhydride (1%)	1.535	320	0.30	VMCH™	Union Carbide	Chlorobenzene
TBOC	<i>t</i> -Butyloxycarbonyl ester of PPHS	1.528	215	0.31	—	—	MIBK*
PVC	Poly(vinyl chloride)	1.533	310	0.33	—	—	Cyclohexanone
PPHS	Poly( <i>p</i> -hydroxy styrene)	1.64	215	0.33	—	Hoechst-Celanese	Methanol
PTFP	Trifluoroacetic acid ester of PPHS	1.492	330	0.36	—	—	Chlorobenzene
SM	Copolymer of styrene and maleic anhydride	1.568	220	0.36	Scripset™ 520	Monsanto	Cyclohexanone
PIM	Polyimide	1.620	215	0.45	Thermid FA7001™	National Starch	Chlorobenzene
PAMS	Poly(α-methyl styrene)	1.592	195	0.47	—	—	Chlorobenzene
PS	Polystyrene	1.592	175	0.50	—	—	Chlorobenzene

\* POMA = propyloxymethylacetate; NMP = N-methylpyrrolidone; MIBK = methylisobutylketone.

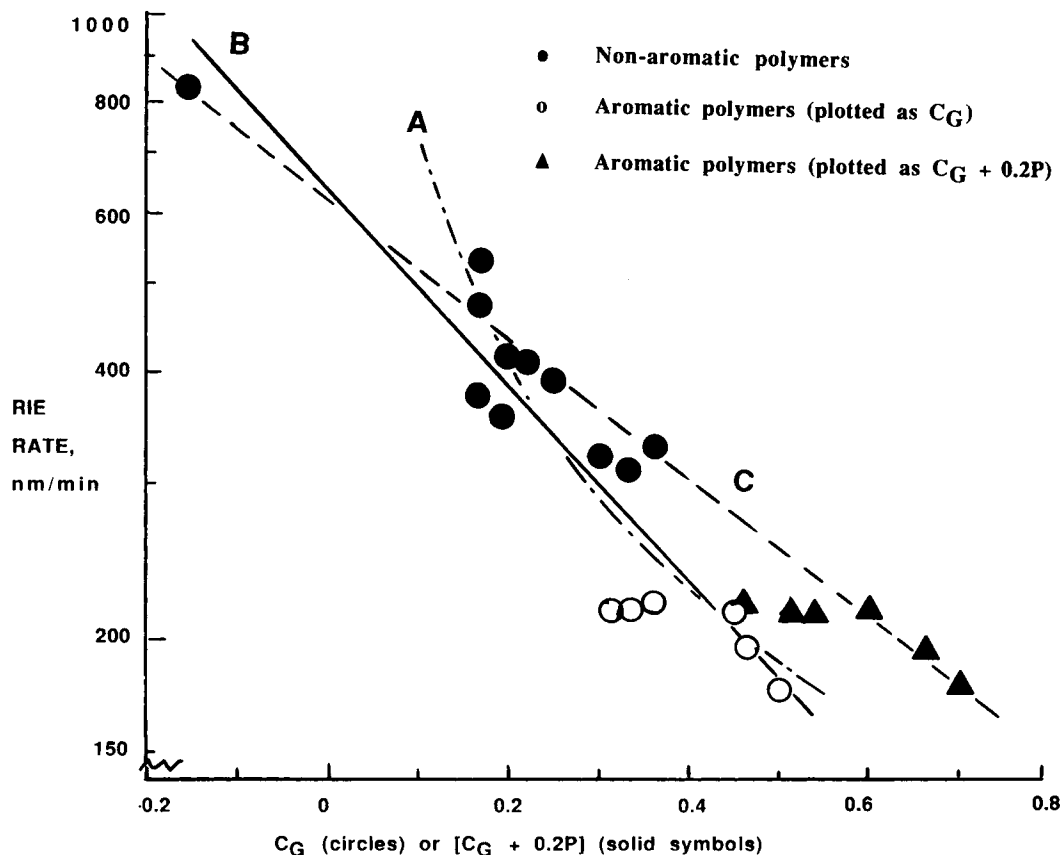
**Table II Polymer Structures (Where the Repeat Unit Is  $-\text{CH}_2-\text{CR}_1\text{R}_2-$  Unless Otherwise Noted)**

	$\text{R}_1$	$\text{R}_2$	Comonomer
CEN	(Typical structure)		
MHB	(Typical structure)		
MHG	(Typical structure)		
PVAc	$-\text{H}$	$-\text{O}-\text{CO}-\text{CH}_3$	Maleic anhydride
AN	$-\text{H}$	$-\text{OCH}_3$	
PMMA	$-\text{CH}_3$	$\text{O}=\text{C}-\text{O}-\text{CH}_3$	Maleic anhydride
PEMA	$-\text{CH}_3$	$\text{O}=\text{C}-\text{O}-\text{CH}_2\text{CH}_3$	
PBMA	$-\text{CH}_3$	$\text{O}=\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$	Maleic anhydride
VMC	(86% vinyl chloride, 13% vinyl acetate, 1% maleic anhydride)		
TBOC	$-\text{H}$	$-\text{C}_6\text{H}_4-\text{O}-\text{CO}-\text{O}-\text{C}(\text{CH}_3)_3$	
PVC	$-\text{H}$	$-\text{Cl}$	
PPHS	$-\text{H}$	$-\text{C}_6\text{H}_4-\text{OH}$	
PTFP	$-\text{H}$	$-\text{C}_6\text{H}_4-\text{O}-\text{CO}-\text{CF}_3$	
SM	$-\text{H}$	$-\text{C}_6\text{H}_5$	Maleic anhydride
PIM			
PAMS	$-\text{CH}_3$	$-\text{C}_6\text{H}_5$	
PS	$-\text{H}$	$-\text{C}_6\text{H}_5$	

efficient of 70 in place of 80) in order to fit the present experimental data better (line A).

One might improve the correlation by taking into account the various contributions of other atoms or

groups. For example, one could improve the fit somewhat by adding to the value of  $C_G$  some arbitrary amount corresponding to the phenyl content. One can add 0.2 to the Gokan parameter for the



**Figure 2** Etch rates in oxygen for polymers of Table I correlated with composition by eq. (2) (curved line A), eq. (4) (line B), and eq. (5) (line C). Power density = 0.25 W/cm<sup>2</sup>.

phenyl-containing monomers (0.1 for the copolymer SM and 0.15 for PIM). The resulting fit (line C in Fig. 2) corresponds to

$$\log [\text{Rate (nm/min)/620}] = -0.78(C_G + 0.2P) \quad (5)$$

where  $P$  is the fraction of phenyl-containing monomers in the copolymer.

Equation (4) is better than eq. (2) for fitting cellulose nitrate, but the reverse is true for some other polymers. For example, Taylor and Wolf<sup>4</sup> reported that poly(butene-1-sulfone) etched three times as fast as did PMMA in an oxygen plasma. Since  $C_G$

for the sulfone is 0.13, it is apparent that eq. (2) would be better than eq. (4).

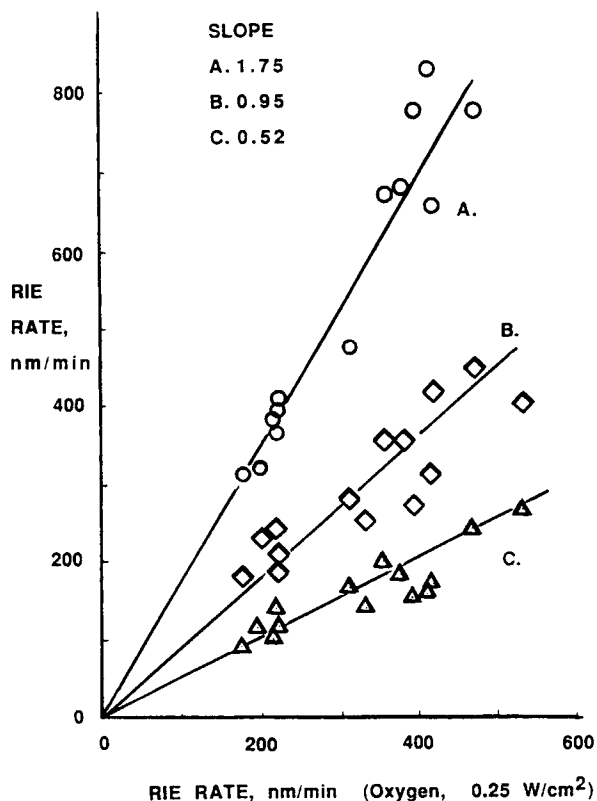
Another comparison to oxygen etch rates that comes to mind is one with flammability ratings. Much work has been reported on the susceptibility of polymers to burning. One of the most popular criteria is the Limiting Oxygen Index (LOI, ASTM D 2863), which is the molar fraction of oxygen needed in the atmosphere around a plastic "candle" to sustain combustion.<sup>14</sup> Although it is true that cel-

**Table III** Plasticizers

Abbrev.	Chemical Name	Supplier	$G_G$
DOS	Di-2-ethylhexyl sebacate	C. P. Hall	0.27
DOP	Di-2-ethylhexyl phthalate	Monsanto	0.30
DBEP	Dibutoxyethyl phthalate	C. P. Hall	0.25

**Table IV** Representative Glass Transition Temperatures<sup>15</sup>

Polymer	% Plasticizer	$T_g$ (°C)
VMCH	0%	85
	50% DOP	< 0
	50% DOS	< 0
PS		105
PS	20% DBEP	45
PMMA		108
PMMA	20% DBEP	70



**Figure 3** Etch rates correlated with low-power (0.25 W/cm<sup>2</sup>) etch rate in oxygen: (A) oxygen, 0.50 W/cm<sup>2</sup>; (B) CF<sub>4</sub>/O<sub>2</sub> (8%), 0.50 W/cm<sup>2</sup>; (C) CF<sub>4</sub>/O<sub>2</sub> (8%), 0.25 W/cm<sup>2</sup>.

lulose nitrate (guncotton) requires almost no oxygen (LOI is almost zero) and burns with explosive force even when confined, the LOI of PMMA and polystyrene are almost identical (0.17–0.18) and the LOI of poly(vinyl chloride) is much higher (0.47). Obviously, these do not jibe with the observed etch rates.

### RIE under Changed Conditions

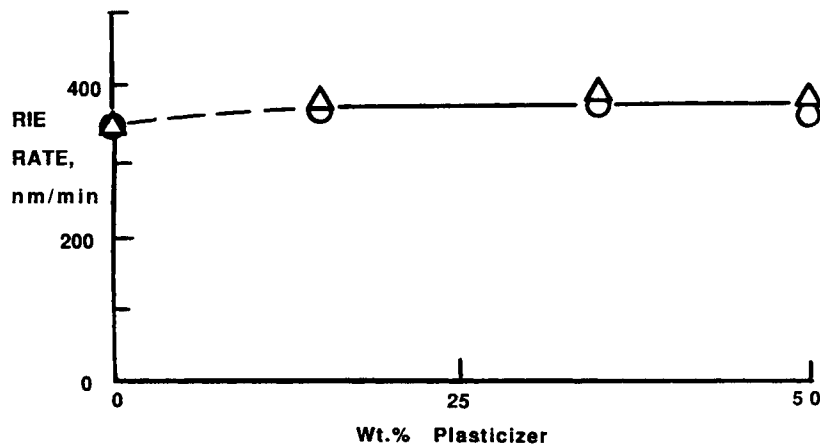
When most of the same polymers were etched at a higher power density (0.50 vs. 0.25 W/cm<sup>2</sup>), the rates tracked those at the low power, being increased by a factor of 1.75 [Fig. 3(A)]. In point of fact, it has been shown that the dependence of the oxygen etch rate is linear in power density but does not go through the origin.<sup>2</sup> Likewise, when the CF<sub>4</sub>/O<sub>2</sub> 8% results at two power densities are compared with the low power density oxygen results, a direct proportionality again is found [Fig. 3(B) and (C)]. This behavior is not unexpected for organic polymers.

### RIE of Plasticized Polymers

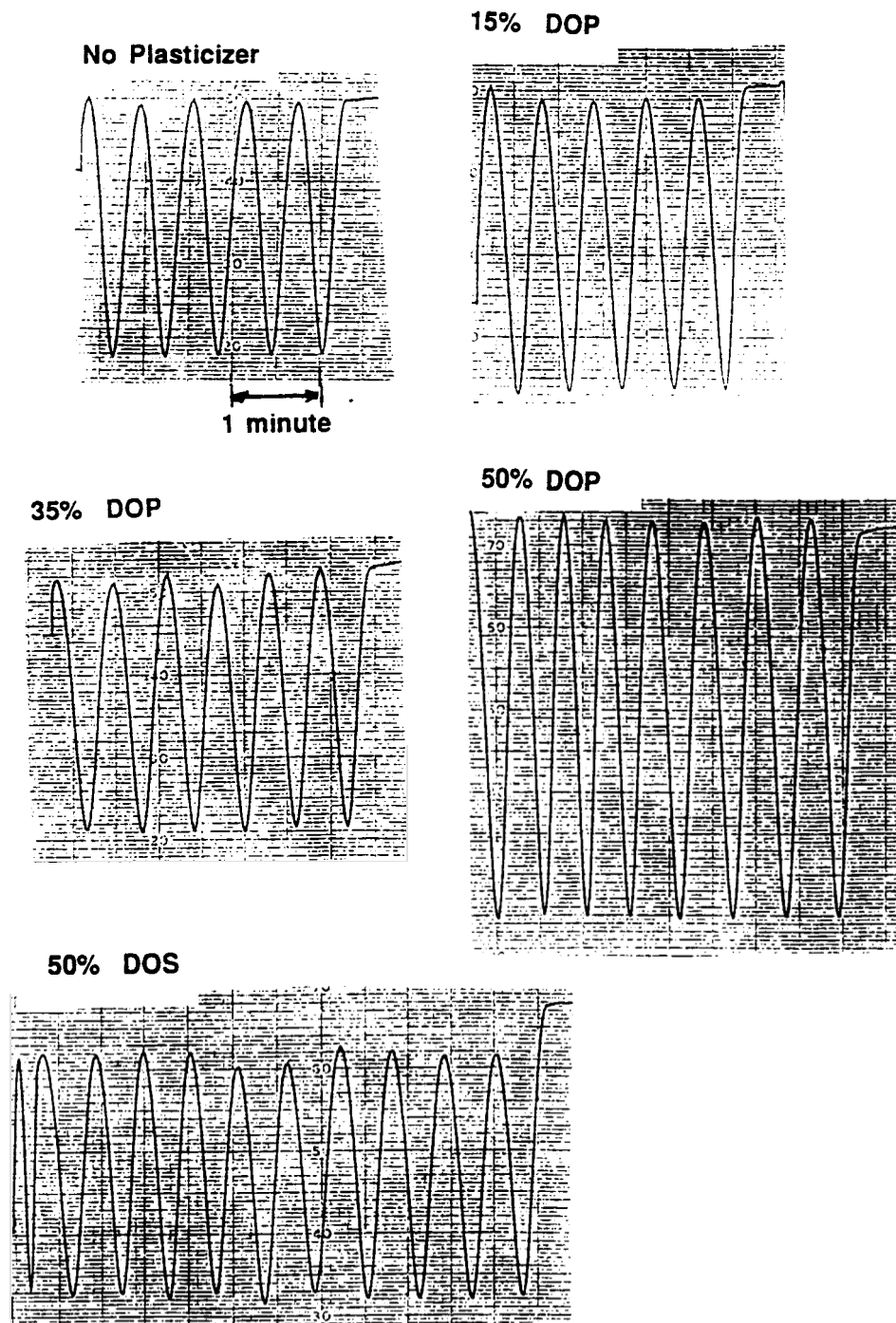
Some workers have interpreted changes in etch rate with temperature as differing above and below the glass transition temperature,  $T_g$ , of a polymer. Plasticization by a small, but nonvolatile compound is a convenient way to change the  $T_g$  of various polymers. For polystyrene, PMMA, and poly(vinyl chloride), the  $T_g$  of the unmodified polymer is well above room temperature. These three were modified by compatible plasticizers to the point of being quite rubbery at room temperature<sup>16</sup> (Tables III and IV).

Poly(vinyl chloride) is remarkably unaffected by plasticization (Fig. 4). (The polymer used by us, VMC, actually is a terpolymer with 13% vinyl acetate and 1% maleic anhydride). However, the interferometer patterns of etching (Fig. 5) are very uniform with either the aliphatic plasticizer (DOS) or the partly aromatic one (DOP). It is to be noted that the values of  $C_G$  for both plasticizers are nearly the same (Table III) and do not differ much from that for the VMC.

The  $C_G$  of DBEP is much lower than that of polystyrene and might be expected to increase its RIE



**Figure 4** Oxygen etch rate of VMC at various plasticizer levels: (Δ) DOS; (○) DOP.



**Figure 5** Reflected light intensity (on ordinate) patterns during the etching of VMC with various amounts of plasticizers. Time scale of the abscissa is the same in each case.

rate. There is, in fact, a slight increase in rate with plasticizer content (Fig. 6). For PMMA, the addition of DBEP lowers the average  $C_G$  and a decrease in etch rate is observed (Fig. 6). In the case of PMMA (with and without plasticizer), the etch rate is not uniform from top to bottom of the film, but accelerates somewhat. This probably is due to the

heating of the substrate with a consequent contribution from thermal depolymerization.<sup>16</sup>

## CONCLUSIONS

The criterion proposed by Gokan et al.<sup>10</sup> continues to yield a good approximation to the etching behav-

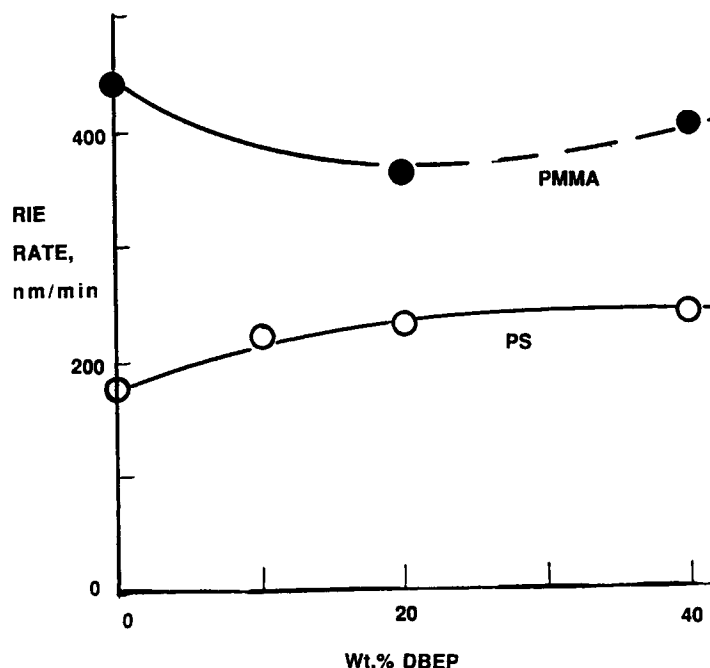


Figure 6 Etch rates of plasticized polymers (in oxygen at 0.25 W/cm<sup>2</sup>).

ior of organic polymers. Thus, there seems to be little likelihood of decreasing etch rates to much lower levels than can be obtained with polystyrene or similar aromatic polymers. Nitrogen, sulfur, and halogens do not seem to alter the generalization.

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