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Reactive Ion Etching of Selected Polymers in O_2 and CF_4/O_2

by

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A series of 17 polymers was etched in RIE mode in oxygen alone and in a mixture of carbon tetrafluoride with oxygen (8% O_2). Rates were monitored using a laser interferometer. The etch rates in oxygen at 0.25 watt/cm^2 fell in the range of 200-300 nm/min for the aromatics (polystyrene and derivatives), 350-450 nm/min for the aliphatics (methacrylates and vinyl acetate), and 500-850 nm/min for the cellulosics (methyl ether and nitrate). At a power density of 0.50 watt/cm^2 the etch rates were about 75 to 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 which lower the T_g 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 compositional effects on etching rate seem to be related to the mole fractions of carbon and oxygen in the resist.

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Reactive Ion Etching of Selected Polymers in O_2 and in CF_4/O_2

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Abstract

A series of 17 polymers was etched in 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_2). The polymers fell into three groups, the aromatics (polystyrene and derivatives), the aliphatics (methacrylates and vinyl acetate), and the cellulosics (methyl ether and nitrate). In oxygen with a power density of 0.25 watt/cm^2, 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 watt/cm^2. The etch rates at the higher power density were about 75 to 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 which 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 of 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.

A-1

Introduction

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

The complex nature of the plasma/surface interactions makes it difficult to achieve a complete understanding of the the degradative mechanisms for polymer resists under "typical" plasma or reactive ion etching (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_2 being a usual concentration)[1]. Oxygen plasmas have been used for a long time for resist stripping. In recent years, however, O_2 RIE has also become an important part of some multilayer resist systems as well as dry-developing schemes based on silyl-derivatization. The fluoride gases have been used for etching silicon and silicon oxide.

Experimental Procedure

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[2]. 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 to 100 milliTorr), gas flow valves, nitrogen backfill for the chamber, and the usual diffusion and roughing pumps. A radio-frequency generator (HFS 2000 D, Plasma-Therm) and an impedance matching network (AMN-2000, Plasma-Therm) power the cathode.

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^2. In all cases the chamber pressure was 40±5 mTorr and gas flow rate was 20 standard cm^3/minute.

Polymer films were spun on 3-inch diameter silicon wafers from 5 to 10% solutions in appropriate solvents. All wafers were baked at 160°C for one hour. The polymers used were either commercially available materials (Tables 1 and 2) or made by us.

In order 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 1).

Results and Discussion

RIE in oxygen at low (0.25 W/cm^2) power density. The polymers tested fall into three groups (Table 1). The aromatics (polystyrene

and derivatives) etch at rates of 200 to 300 nm/min. The aliphatic polymers (based on methacrylates and vinyl acetate) etch more rapidly, 350 to 450 nm/min. The cellulose-based polymers etch more rapidly still, 500 to 850 nm/min.

There have been a number of studies in which a variety of chemical structures have been classified as to etching rate[3-13]. Most workers agree that polymers containing aromatic rings resist etching more than aliphatic polymers. Anderson[2] among others found an almost linear relationship between etching rate in oxygen with aromatic content with PMMA (poly(methyl methacrylate)) and poly(alpha-methyl styrene) at the extremes.

Gokan[10,11] et al 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

$$N_T/(N_C - N_O) \qquad (1)$$

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

$$\text{Etch rate (nm/min)} = 50 + 80\{N_T/(N_C - N_O)\} \qquad (2)$$

It is obvious that in a polymer where equal numbers of carbon and oxygen atoms are present such as poly(oxymethylene) 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 versus composition expressed as C_G is more satisfactory (Fig. 2) where the ratio proposed by Gokan now is

$$C_G = (N_C - N_O)/N_T \qquad (3)$$

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 ±30% of the line corresponding to

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

Also shown is equation (2) adjusted slightly (with a coeffic'ent of 70 in place of 80) in order to fit the present experimental .ta better .

One might improve the correlation by taking into account the various contributions of other atoms or groups. But the amount of data probably does not warrant much greater analysis. Eq. 4 is better than Eq. 2 for fitting cellulose nitrate, but the reverse is true for some other polymers. For example, Taylor and Wolf[4] reported that poly(butene-1-sulfone) etched three times as fast as 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[14]. While it is true that cellulose 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 versus 0.25 W/cm^2), the rates tracked those at the low power, being increased by a factor of 1.75 (Fig. 3A). In point of fact, it has shown that the dependence of oxygen etch rate is linear in power density but does not go through the origin[2]. Likewise, when the CF_4/O_2 8% results at two power densities are compared with the low power density oxygen results, a direct proportionality again is found (Fig. 3B and 3C). 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 non-volatile 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 (Tables 3 and 4).

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 3) 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 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[15].

Conclusions

The criterion proposed by Gokan[10] continues to yield a good approximation to the etching behavior 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. Of course, certain other elements, notably silicon and tin among others, can enhance etch resistance greatly[2].

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Figure Captions:

1. Sketch of RIE apparatus showing position of laser interferometer.

2. Etch rates in oxygen for polymers of Table 1 correlated with composition by Eq. 2 (dashed line) and Eq. 4 (solid line). Power density = 0.25 W/cm^2.

3. Etch rates correlated with low power (0.25 W/cm^2) etch rate in oxygen. A. Oxygen, 0.50 W/cm^2; B. CF_4/O_2(8%), 0.50 W/cm^2; C. CF_4/O_2(8%), 0.25 W/cm^2.

4. 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.

5. Oxygen etch rate of VMC at various plasticizer levels. (+), DOS; (o), DOP.

6. Etch rates of plasticized polymers (in oxygen at 0.25 W/cm^2).

Table 1 Polymers (etched in oxygen at 0.25 W/cm^2)

Abbrev.	Composition	Refractive Index	Etch Rate, nm/min	CC	Trade name	Commercial source	Spinning solvent
PMMA	Poly(methyl methacrylate)	1.489	415	0.20	-------------	-------------	chlorobenzene
PEMA	Poly(ethyl methacrylate)	1.485	410	0.22	-------------	-------------	chlorobenzene
PBMA	Poly(n-butyl methacrylate)	1.483	390	0.25	-------------	-------------	chlorobenzene
PS	Polystyrene	1.592	175	0.50	-------------	-------------	chlorobenzene
AN	Copolymer of vinyl methyl ether and maleic anhydride	1.47	355	0.19	Gantrez AN™	GAF	NMP*
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
PPHS	Poly(p-hydroxy styrene)	1.64	215	0.33	-------------	Hoechst-Celanese	methanol
PVC	Poly(vinyl chloride)	1.533	310	0.33	-------------	-------------	cyclohexanone
VMC	Terpolymer of vinyl chloride (86%), vinyl acetate (13%), maleic anhydride (1%)	1.535	320	0.30	VMCH™	Union Carbide	chlorobenzene
CEN	Cellulose nitrate	1.50	835	-0.15	-------------	-------------	POMA*
PVAc	Poly(vinyl acetate)	1.467	375	0.17	-------------	-------------	cyclohexanone
PAMS	Poly(alphamethyl styrene)	1.592	195	0.47	-------------	-------------	chlorobenzene
TBOC	t-butyloxycarbonyl ester of PPHS	1.528	215	0.31	-------------	-------------	MIBK*
MHB	Methoxycellulose (w/ butoxy)	1.470	530	0.17	Methocel™ HB	Dow	water
MHG	Methoxycellulose (w/propoxy)	1.502	470	0.17	Methocel™ HG	Dow	water
PTFP	Trifluoroacetic acid ester of PPHS	1.492	330	0.36	-------------	-------------	chlorobenzene

*NMP = N-methyl pyrrolidone; POMA = propyloxymethylacetate; MIBK = methylsiobutylketone

Table 2 Polymer Structures (where the repeat unit is $-CH_2-CR_1R_2-$ unless otherwise noted)

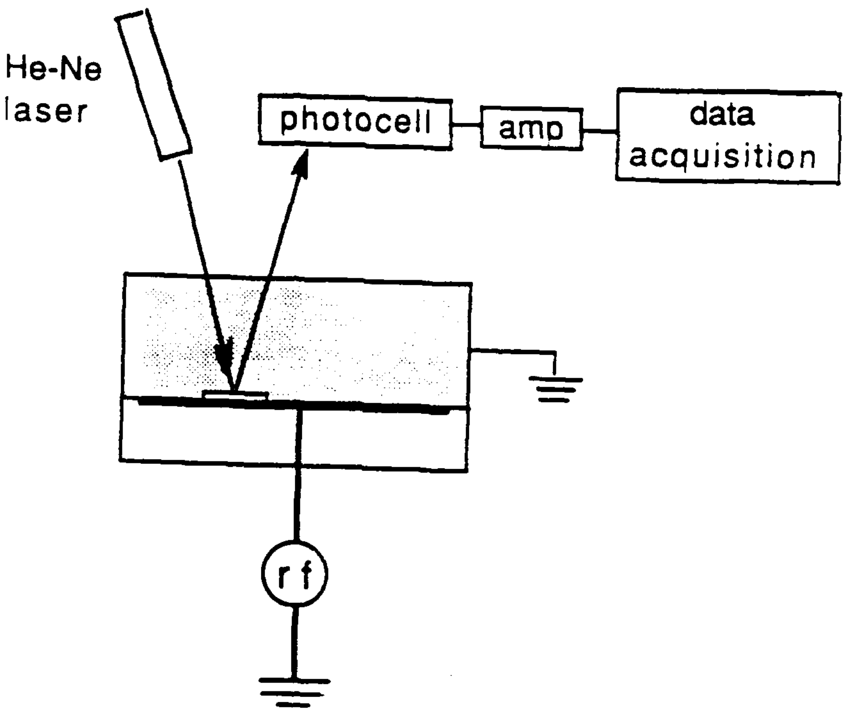
	R_1	R_2	Comonomer
PMMA	$-CH_3$	$O=C-O-CH_3$	
PEMA	$-CH_3$	$O=C-O-CH_2CH_3$	
PBMA	$-CH_3$	$O=C-O-CH_2CH_2CH_2$	
PS	-H	$-C_6H_5$	
AN	-H	$-OCH_3$	maleic anhydride
SM	-H	$-C_6H_5$	maleic anhydride
PIM			
PPHS	-H	$-C_6H_4-OH$	
PVC	-H	-Cl	
VMC	(86% vinyl chloride, 13% vinyl acetate, 1% maleic anhydride)		
CEN	(typical structure)		
PVAc	-H	$-O-CO-CH_3$	
PAMS	$-CH_3$	$-C_6H_5$	
TBOC	-H	$-C_6H_4-O-CO-O-C(CH_3)_3$	
MHB	(typical structure)		
MHG	(typical structure)		
PTFP	-H	$-C_6H_4-O-CO-CF_3$	

Table 3 Plasticizers

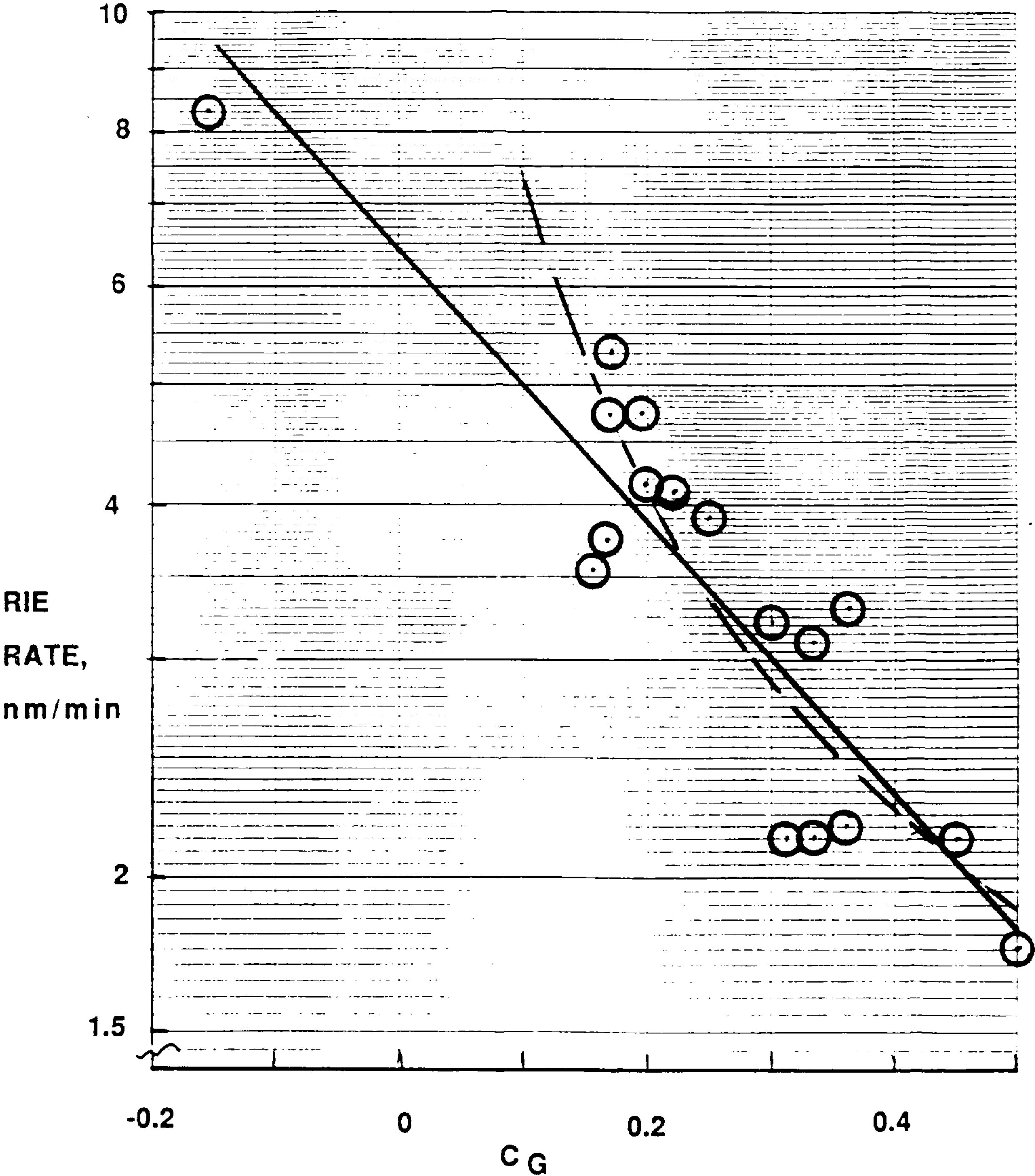
Abbrev.	Chemical name	Supplier	C_G
DOS	Di-2-ethylhexyl sebacate	C. P. Hall	0.27
DOP	Di-2-ethylhexyl phthalate	Monsanto	0.30
DBEP	Di-butoxyethyl phthalate	C. P. Hall	0.25

Table 4 Representative Glass Transition Temperatures[16]

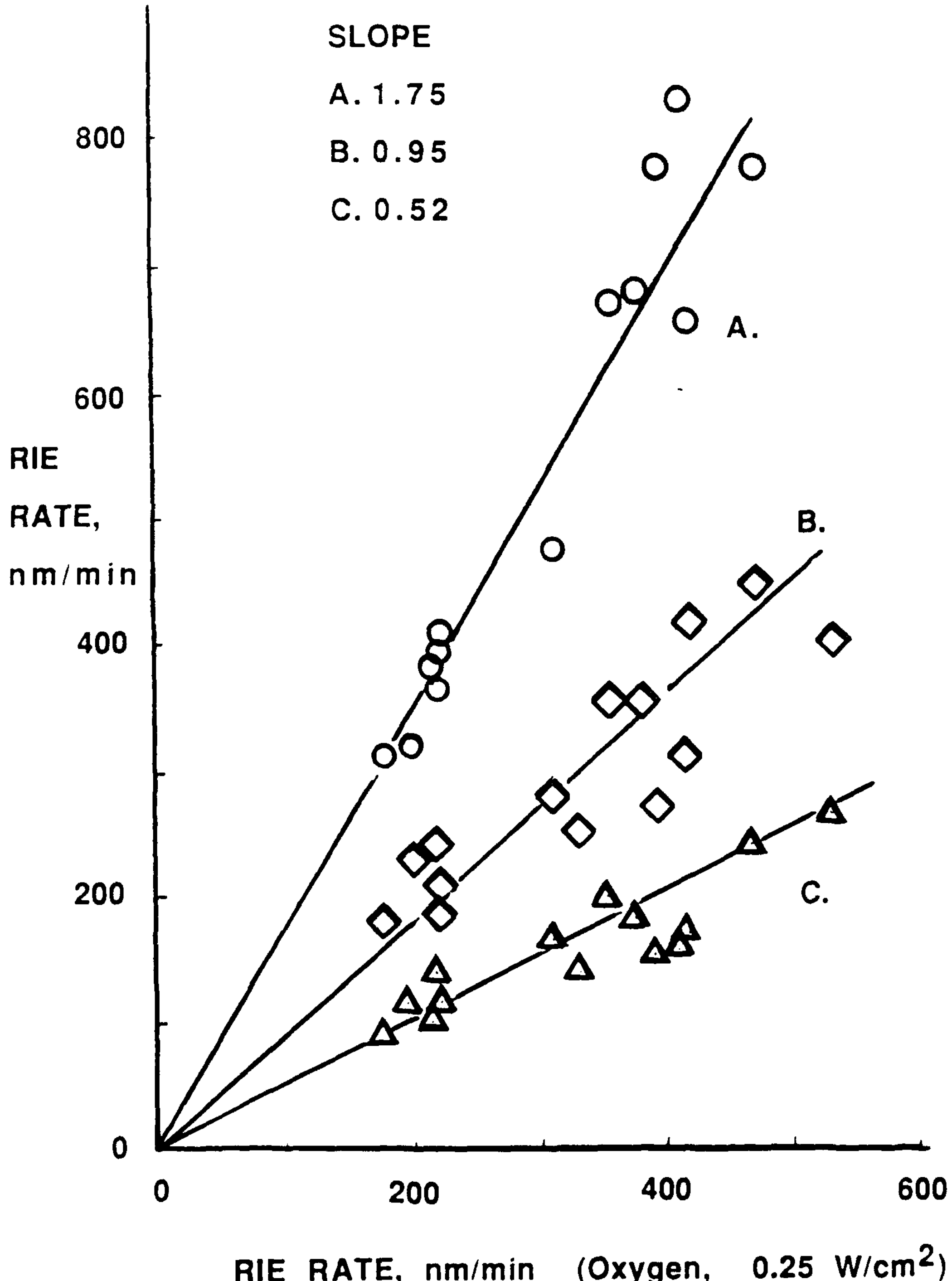
Polymer	% plasticizer	T_g, °C
VMCH	0	85
	50% DOP	< 0
	50% DOS	< 0
PS		105
PS	20% DBEP	45
PMMA		108
PMMA	20% DBEP	70



1. Sketch of RIE apparatus showing position of laser interferometer.



2. Etch rates in oxygen for polymers of Table 1 correlated with composition by Eq. 2 (dashed line) and Eq. 4 (solid line). Power density = 0.25 W/cm^2.



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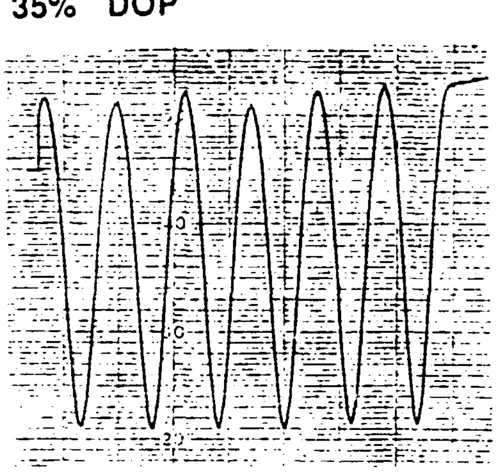
4. Reflected light intensity (on ordinate) patterns during the etching of VMC with various amounts of plasticizers. Time scale of the abscissa is the same in each case.

No Plasticizer

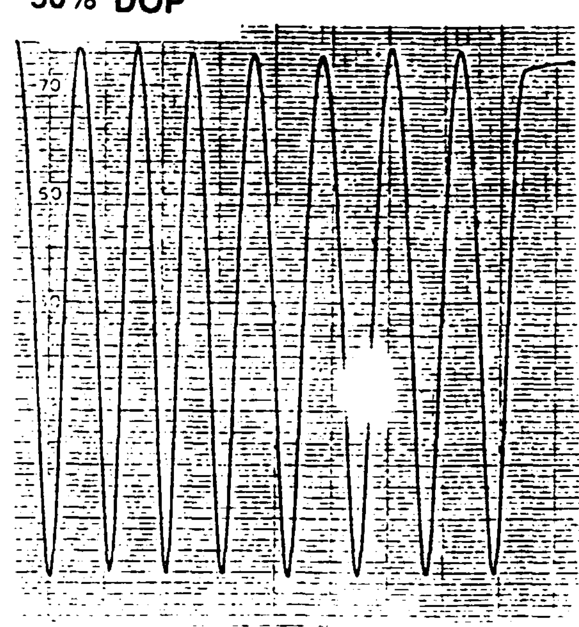
1 minute

15% DOP

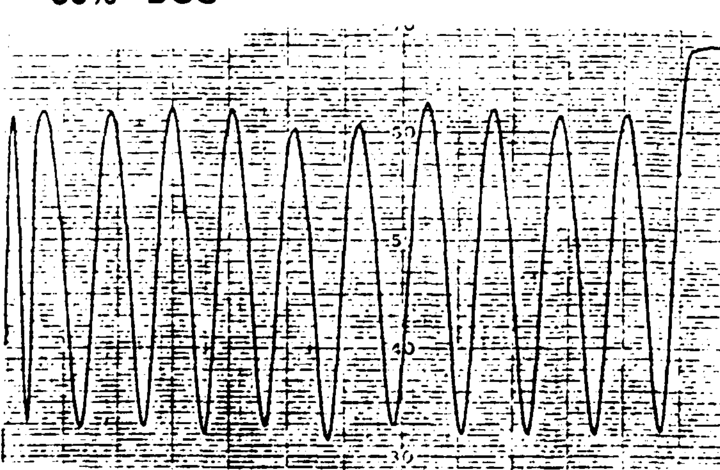
35% DOP



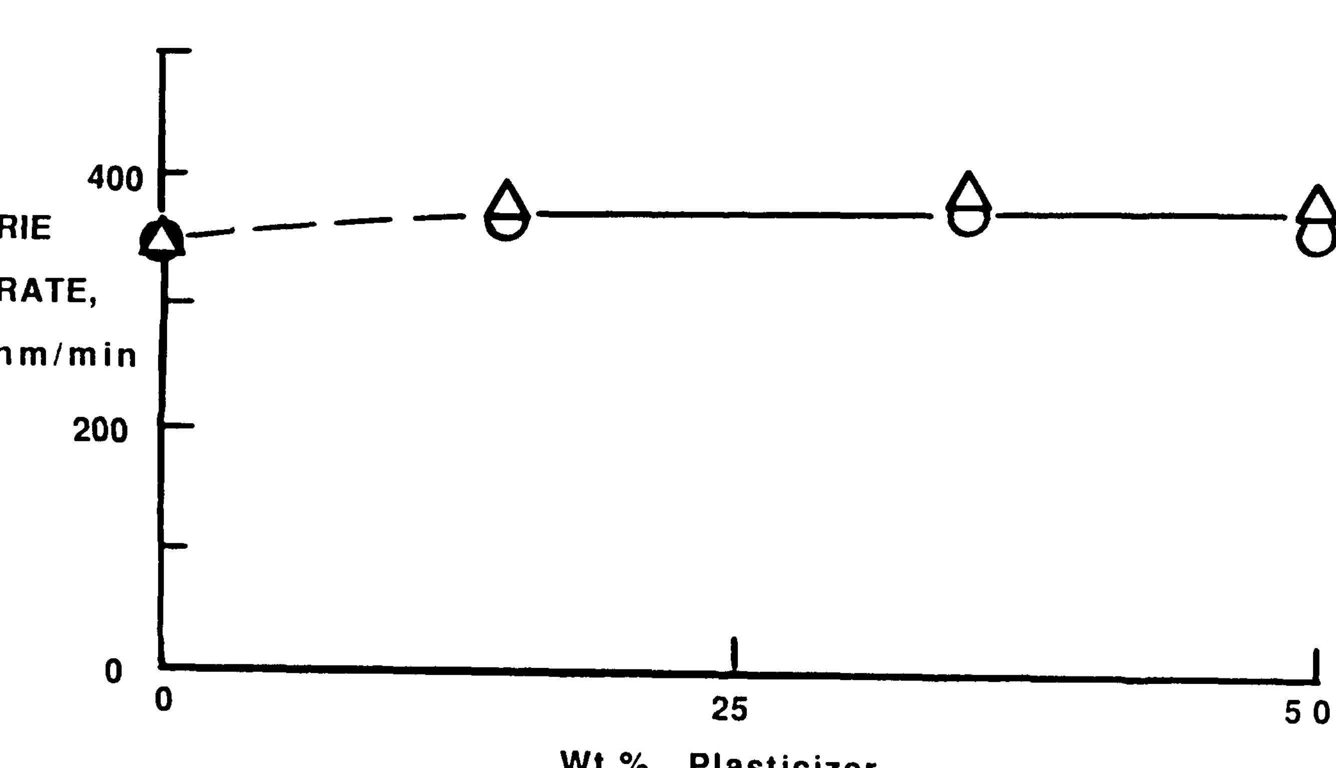
50% DOP

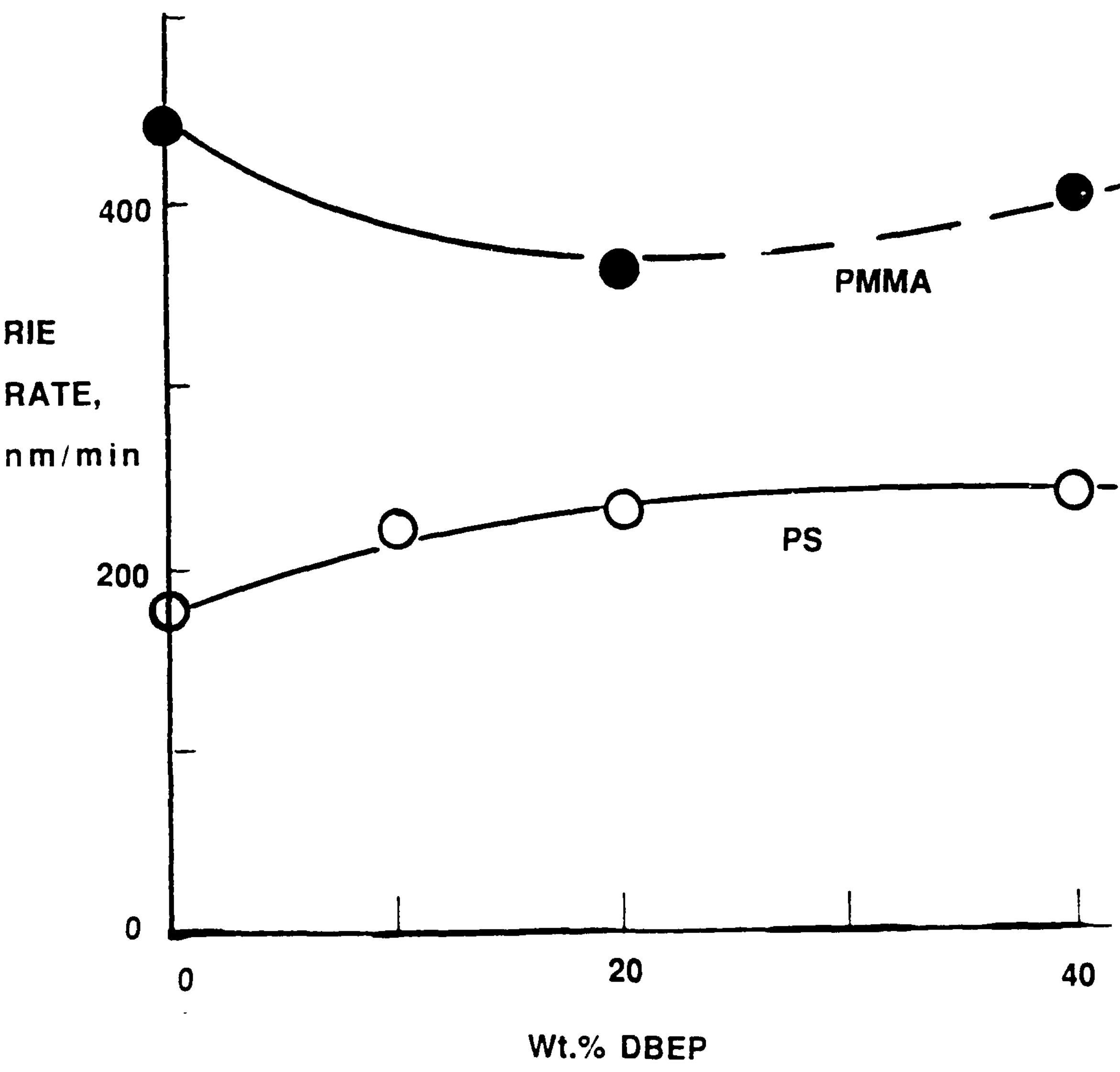


50% DOS



5. Oxygen etch rate of VMC at various plasticizer levels. (Δ), DOS; (o), DOP.





6. Etch rates of plasticized polymers (in oxygen at 0.25 W/cm^2).

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