

# Dry Etching Durability of Positive Electron Resists

KATSUHIRO HARADA, *Nippon Telegraph and Telephone Public Corporation, Ibaraki Electrical Communication Laboratory, Tokai, Ibaraki, 319-11, Japan*

## Synopsis

The effects of positive electron resist structures and  $G$  values for scission on dry etching durability have been studied with regard to plasma etching, reactive sputter etching, and plasma ashing. Polymers of aromatic methacrylates, especially poly( $\alpha$ -methylstyrene), all of which contain a benzene ring in the side chain, exhibit superior durability for each etching system. On the other hand, polymers of fluorinated and chlorinated methacrylates show low durability compared with the nonsubstituted polymethacrylates. In addition, they vary in durability with respect to the etching gas used. The sputtering effect which is induced by ion bombardment in flat bed-type reactors produces a significant loss in thickness of positive resists. Rough correlations between dry etching rates and  $G_s$ (scission) as the indication of sensitivity were obtained. The large dispersion of the correlations implies the possibility of more useful positive electron resists of high durability and high sensitivity.

## INTRODUCTION

Dry etching,<sup>1,2</sup> which make possible transfer of high-resolution patterns to a variety of substrates, displays highly versatile performances in microfabrication, i.e., anisotropic etching without undercutting, selective etching of substrates, and control over the exact shape of the etching profile. The development of this technique, accompanied by developments in electron beam and X-ray lithography, is accelerating the shrink of line width and length of patterns for microfabrication.

The resists used in dry etchings must fundamentally have high dry etching durability with high resolution and high sensitivity for such radiations. A highly durable negative resist, chloromethylated polystyrene (CMS), which has high resolution and high sensitivity, has been developed.<sup>3,4</sup> However, the development of a highly durable positive resist with high sensitivity is very difficult, because both parameters (high resolution and high sensitivity) may depend on the ease of the main chain decomposition. In positive resists, these parameters tend to conflict with each other.

Resist durability is influenced primarily by dry etching conditions. The author previously reported the effects of some etching conditions on positive resist durability and decomposition mechanisms using PMMA.<sup>5</sup>

In the present work, the relation between the polymer structure of a positive resist and its durability and the change in durability with some etching systems were examined.

## EXPERIMENTAL

## Preparations of Positive Resists

It is well known that polymethacrylates are easily degraded by radiation. Many kinds of polymethacrylates, their derivatives, and their copolymers have been reported as positive resists used for electron beam and X-ray lithography.<sup>6</sup> Therefore, a variety of polymethacrylate esters were selected to estimate positive resist durability. Some nonmethacrylate polymers were also used for comparison. They are shown in Table I with their molecular weights.

PMMA<sup>7</sup> (Elvacite 2041, du Pont), FBM<sup>8</sup> (Daikin Kogyo), and FPM<sup>9</sup> (Daikin Kogyo) were commercially available resists. PEtMA, PnBuMA, PiBuMA, PtBuMA, PBzMA, PMIPK, and PME<sub>2</sub>IA were obtained by ordinary radical polymerization from the commercial monomer. PBS and P $\alpha$ MeSt were polymerized at  $-78^{\circ}\text{C}$  by initiation with *tert*-butyl hydroperoxide<sup>10</sup> and nBuLi, respectively.

The monomers of PCl<sub>3</sub>EtMA, PF<sub>3</sub>EtMA, PPhMA, PPhPrMA, PFPhMA, PCl<sub>3</sub>PhMA, and PCF<sub>3</sub>PhMA were synthesized by reacting methacryloyl chloride with the corresponding alcohol in pyridine in a similar manner as reported for  $\beta$ -phenyl *n*-propylmethacrylate.<sup>11</sup> These monomers were also polymerized by ordinary radical polymerization.

TABLE I  
Specifications of Polymers Used for Positive Resist

Sample	Polymer name	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Heat treatment temperature, $^{\circ}\text{C}^c$
PMMA	Poly(methyl methacrylate) <sup>a</sup>	44.3	2.8	170
PEtMA	Poly(ethyl methacrylate)	35.8	1.8	140
PnBuMA	Poly(butyl methacrylate)	126	3.0	140
PiBuMA	Poly(isobutyl methacrylate)	53.1	2.0	140
PtBuMA	Poly( <i>tert</i> -butyl methacrylate)	108	1.9	140
PCl <sub>3</sub> EtMA	Poly(2,2,2-trichloroethyl methacrylate)	114	2.0	140
PF <sub>3</sub> EtMA	Poly(2,2,2-trifluoroethyl methacrylate)	148	2.4	140
FPM	Poly(1,1-dimethyl-2,2,3,3-tetrafluoropropyl methacrylate) <sup>b</sup>	87.3	2.4	170
FBM	Poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) <sup>b</sup>	116	2.4	140
PPhMA	Poly(phenyl methacrylate)	95.6	4.9	170
PFPhMA	Poly( <i>p</i> -fluorophenyl methacrylate)	384	4.1	170
PCl <sub>3</sub> PhMA	Poly(2,4,6-trichlorophenyl methacrylate)	8.0	2.1	170
PCF <sub>3</sub> PhMA	Poly( <i>m</i> -trifluoromethyl methacrylate)	11	2.6	170
PMeOPhMA	Poly( <i>p</i> -methoxyphenyl methacrylate)	—	—	170
PBzMA	Poly(benzyl methacrylate)	124	2.2	170
PMeOBzMA	Poly( <i>p</i> -methoxybenzyl methacrylate)	9.6	2.7	170
PPhPrMA	Poly(3-phenylpropyl methacrylate)	4.9	2.2	140
P $\alpha$ MeSt	Poly( $\alpha$ -methylstyrene)	165	1.2	170
PMIPK	Poly(methyl isopropenyl ketone)	11.7	1.9	100
PME <sub>2</sub> IA	Poly(dimethyl itaconate)	5.4	1.7	140
PBS	Poly(butene-1 sulfone)	122	6.5	100

<sup>a</sup> Elvacite 2041 (du Pont).

<sup>b</sup> Daikin Kogyo.

<sup>c</sup> Samples were baked for 30 min in film state before use to remove the spinning solvent.

The molecular weights of the resists in Table I were measured by gel permeation chromatography (GPC) (HLC-802UR, Toyo Soda Kogyo) using tetrahydrofuran as solvent, except for FBM and FPM, where methyl ethyl ketone was used.

Dry etching durabilities were estimated with thin films about 1  $\mu\text{m}$  thick. The thin films were prepared on thermally oxidized silicon wafers using the standard spin-coating technique from solutions of the resist. Then they were baked in air for 30 min at the temperature given in Table I in order to remove the spinning solvent.

### Dry Etching

Two dominant factors contributed to the resist durability in dry etching conditions. One was the kind of active species such as chlorine or fluorine radicals and atomic oxygen which could decompose the resist. This factor depends on the etching gas used. The fluorinated and chlorinated organic and inorganic gases, i.e.,  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_3\text{F}_8$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_4$ ,  $\text{SiF}_4$ , etc., are widely used corresponding to the kind of substrate processed.<sup>1,2</sup> Additive gases such as  $\text{O}_2$ ,  $\text{H}_2$ , and Ar are injected into the etching gas in order to increase the etching rate of the substrates and the etching rate ratio of the substrates to the resists. It is important to clarify the influence of gases containing chlorine, fluorine, and oxygen on resist durability because the chlorine and fluorine radicals and atomic oxygen produced in these gas plasmas have high and different chemical activities. Typical and fundamental etching gases,  $\text{CF}_4 + 5\% \text{O}_2$ ,  $\text{CCl}_4$ , and  $\text{O}_2$  in Table II, were applied to current work.

The other factor is the sputtering effect, which is caused by bombardment by accelerated ions produced by a discharge. This factor depends on the etching system, which may be classified broadly into two types: tunnel and flat-bed reactors. A tunnel reactor with a perforated shield can be used to eliminate the sputtering effect completely.<sup>12</sup> With the flat-bed reactor, the resist is exposed to bombardment by ions<sup>12</sup> and could thus be etched by sputtering.

Four etching systems (Table II) were therefore selected and examined for each positive resist. A capacity coupling tunnel reactor was used for  $\text{CF}_4/\text{O}_2$  plasma etching and plasma ashing. For plasma etching and plasma ashing, a perforated shield and a glass sample stage<sup>5</sup> designed to maintain the sample at constant temperature were applied to the tunnel reactor. The perforated shield and mild rf power for plasma ashing are applied in order to obtain durability estimation of high precision.

Commercially available flat-bed reactors were used for  $\text{CF}_4/\text{O}_2$  reactive sputter etching ( $\text{CF}_4$ -RSE) and  $\text{CCl}_4$  reactive sputter etching ( $\text{CCl}_4$ -RSE).

The dry etching durabilities of resists were estimated by their etching rates at given etching conditions, that is, a low etching rate is synonymous with high durability, and vice versa.

The depth etched into the resists was measured by a Talystep (Taylor-Hobson). The relationship of etching depth to etching time is not necessarily linear. Certain resists in plasma etching showed a decreasing etching rate with time. In these cases, the etching rates were represented by the tangent of the etching depth to etching time curve passing through the origin.

TABLE II  
Specifications of Etching Systems Used to Estimate Dry Etching Durability of Positive Resists

Etching system	Reactor type	Etching gas	Applied power	Etching temperature, °C	Typical etching rate for substrate, Å/min
Plasma etching	tunnel (simultaneous use of perforated shield) IPC-2005	CF <sub>4</sub> + 5% O <sub>2</sub> (100 cm <sup>3</sup> /min, 0.75 torr)	13.56 MHz 200 W	60 (simultaneous use of glass sample stage <sup>a</sup> )	SiO <sub>2</sub> ; 120
Plasma ashing	"	O <sub>2</sub> (50 cm <sup>3</sup> /min, 1.0 torr)	13.56 MHz 100 W	"	PMMA; 320
CF <sub>4</sub> -Reactive sputter etching (CF <sub>4</sub> -RSE)	flat-bed DEM-451	CF <sub>4</sub> + 5% O <sub>2</sub> (10 sccm, 60 m torr)	13.56 MHz 150 W	—	SiO <sub>2</sub> ; 400
CCl <sub>4</sub> -Reactive sputter etching (CCl <sub>4</sub> -RSE)	flat-bed PLASMA FAB-317	CCl <sub>4</sub> (75 sccm, 0.25 torr)	380 kHz (3 A)	—	Al + 2%Si; 5000 Å/5 min

<sup>a</sup> See text.

### Radiation $G$ Value for Scission

The sensitivity of positive resists to electron beam and X-ray exposure is related to both the radiation  $G$  value for scission and selective solubility of irradiated resists from unirradiated resists.<sup>13</sup> The  $G$ (scission) of positive resists is the primary indication of sensitivity for such radiations. A high  $G$ (scission) implies a highly sensitive resist but it also implies low durability for dry etching.

In order to discuss the correlation between sensitivity and dry etching durability, the  $G$ (scission) values were measured. Such values have been reported for some positive resists. However, discrepancies in the values are recognized in the literatures, probably because of differences in conditions such as irradiation and molecular weight measurements. The  $G$ (scission) values for our positive resist have therefore been estimated under the same conditions.

The resists in powder state were sealed under vacuum into glass tubes. The tubes were irradiated by  $\gamma$ -rays (<sup>60</sup>Co) at room temperature for 40 days at dosages ranging from 2 to 10 Mrad. The  $\bar{M}_n$  values of the original and irradiated resists were measured by GPC described above. The  $G$ (scission) values were determined from the inverse number-average molecular weight,  $1/\bar{M}_n$ , vs.  $\gamma$ -radiation dosage.<sup>7</sup>

## RESULTS AND DISCUSSION

### Effects of Structure on Dry Etching Durability of Positive Resists

Tables II, III, and IV show the dry etching rates with respect to four etching systems for four groups of positive resists, i.e., polymers of alkyl methacrylate, polymers of aromatic methacrylate and P $\alpha$ MeSt, polymers of chlorinated and fluorinated methacrylates, and nonmethacrylate polymers. Some resists in each group are displayed by an Arrhenius plot for plasma etching accompanying that of PMMA. They are shown in Figures 1, 2, 3, and 4.

### Polymers of Alkyl Methacrylate

Polymers of alkyl methacrylate did not show much difference in their durabilities with regard to alkyl structures and etching systems, except that PBuMA showed a relatively small etching rate in plasma etching and CCl<sub>4</sub>-RSE.

TABLE III  
Dry Etching Durabilities of Polymers of Alkyl Methacrylate<sup>a</sup>

Sample	Resist etching rate, Å/min			
	Plasma etching	Plasma ashing	CF <sub>2</sub> -Reactive sputter etching	CCl <sub>4</sub> -Reactive sputter etching
PMMA	52 (1.0)	320 (1.0)	760 (1.0)	1700 (1.0)
PEtMA	57 (1.1)	360 (1.1)	1050 (1.4)	2200 (1.3)
PnBuMA	35 (0.7)	330 (1.0)	960 (1.3)	1200 (0.7)
PiBuMA	29 (0.6)	380 (1.2)	950 (1.3)	1200 (0.7)
PtBuMA	29 (0.6)	360 (1.1)	890 (1.2)	1200 (0.7)

<sup>a</sup> Values in parentheses are the etching rate ratios of each resist to PMMA in each etching system.

TABLE IV  
Dry Etching Durabilities of Polymers of Aromatic Methacrylate and P $\alpha$ MeSt<sup>a</sup>

Sample	Resist etching rate, Å/min			
	Plasma etching	Plasma ashing	CF <sub>4</sub> -Reactive sputter etching	CCl <sub>4</sub> -Reactive sputter etching
PPhMA	16 (0.3)	210 (0.7)	360 (0.5)	990 (0.6)
PBzMA	20 (0.4)	210 (0.7)	390 (0.5)	1100 (0.7)
PPhPrMA	22 (0.4)	190 (0.6)	390 (0.5)	850 (0.5)
PMeOPhMA	18 (0.3)	220 (0.7)	330 (0.4)	980 (0.6)
PMeOBzMA	13 (0.3)	210 (0.7)	460 (0.6)	1100 (0.7)
P $\alpha$ MeSt	9 (0.2)	170 (0.5)	350 (0.5)	520 (0.3)

<sup>a</sup> Values in parentheses are the etching rate ratios of each resist to PMMA in each etching system.

The Arrhenius plots of the etching rates for the plasma etching as shown in Fig. 1 deviated markedly from linearity above about  $T_g$  where the etching rates rapidly accelerated. The same results were reported previously for PMMA.<sup>5</sup> Below these bent points, decomposition occurs predominantly by random chain scission. According to the rise of temperature from the bent point, depropagation followed by random chain scission contributes largely to decomposition. The bent points of each plot in Fig. 1 are observed about 20°C below  $T_g$  ( $T_g$  is 104°C for PMMA,<sup>14</sup> 66°C for PEtMA,<sup>14</sup> 19°C for PnBuMA,<sup>14</sup> 53°C for PiBuMA,<sup>14</sup> and 107°C for PtBuMA,<sup>15</sup>). This has similarly been considered for PMMA.<sup>5</sup> The relatively large plasma etching rate of PEtMA in Table I could therefore be due to the temperature effects because the plasma etching rates in Table I were measured at 60°C. The durabilities for plasma etching, in the order butyl, ethyl, and methyl-methacrylate, were obtained at 40°C (Fig. 1).

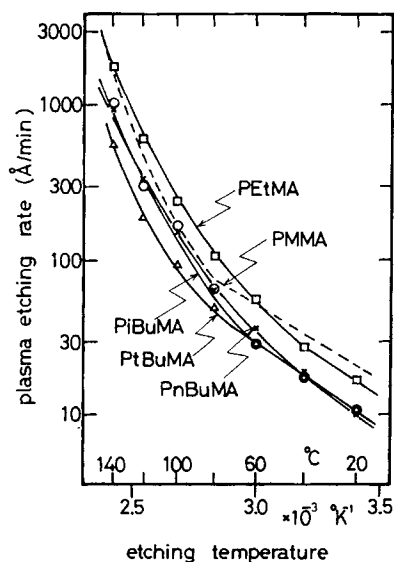


Fig. 1. Etching rates of polymers of alkyl methacrylate in plasma etching as function of temperature. Gas, CF<sub>4</sub> + 5% O<sub>2</sub>; gas flow rate, 100 cm<sup>3</sup>/min; rf power, 200 W.

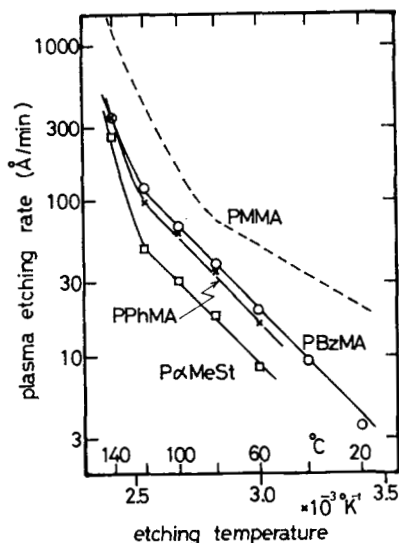


Fig. 2. Etching rates of polymers of aromatic methacrylate and PαMeSt in plasma etching as function of temperature. Gas, CF<sub>4</sub> + 5% O<sub>2</sub>; gas flow rate, 100 cm<sup>3</sup>/min; rf power, 200 W.

*Polymers of Aromatic Methacrylate and PαMeSt*

Polymers of aromatic methacrylate and PαMeSt show high durability for each etching system compared with other polymethacrylates. PαMeSt especially reveals superior durability. There are no significant differences of durability among polymers of aromatic methacrylate. The effects of substituted methoxy groups on durability are very small in PMeOPhMA and PMeOBzMA. High durability is due to the existence of benzene rings in the polymers and can be explained by the so-called protective effect which is due to the presence of phenyl groups within a polymer molecule.<sup>16</sup>

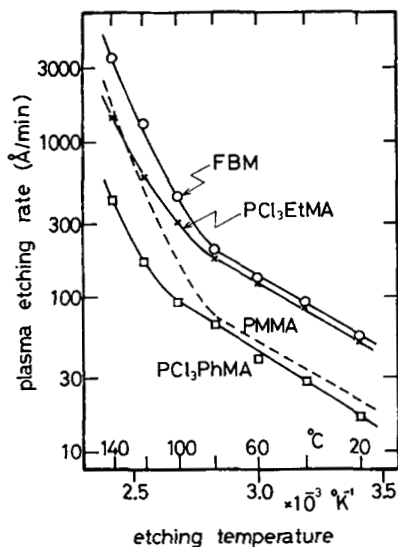


Fig. 3. Etching rates of polymers of chlorinated and fluorinated methacrylate in plasma etching as function of temperature. Gas, CF<sub>4</sub> + 5% O<sub>2</sub>; gas flow rate, 100 cm<sup>3</sup>/min; rf power, 200 W.

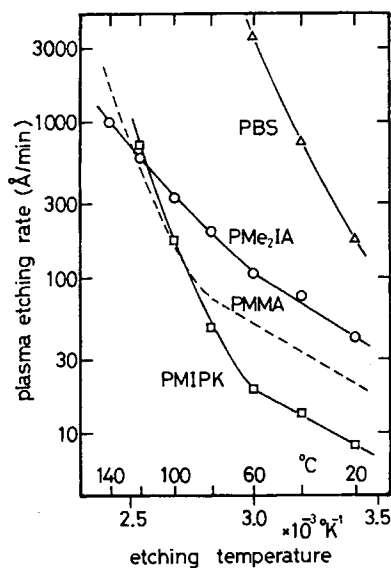


Fig. 4. Etching rates of nonmethacrylate polymers in plasma etching as function of temperature. Gas,  $\text{CF}_4 + 5\% \text{O}_2$ ; gas flow rate,  $100 \text{ cm}^3/\text{min}$ ; rf power, 200 W.

The Arrhenius plots of these resists, as shown in Fig. 2, give the same, relatively large activation energies (7.7 kcal/mol) compared with that of PMMA (4.4 kcal/mol) in the linear region. These magnitudes of the activation energy suggest diffusion control; however, somewhat large activation energies of polymers of aromatic methacrylate could depend on small  $G$  (scission) values described later. In the linear region, the rate of main-chain scission is almost in competition with diffusion of active species. This has also been recognized by the previous results.<sup>5</sup> When the amount of active species is decreased by reducing rf power, the activation energy of PMMA etching rates increases in the same linear region as shown in Fig. 2. All Arrhenius plots bend at about  $120^\circ\text{C}$ , independent of their  $T_g$  ( $T_g$  of PBzMA,  $54^\circ\text{C}$ <sup>15</sup>; of PPhMA,  $110^\circ\text{C}$ <sup>15</sup>; of P $\alpha$ MeSt,  $180^\circ\text{C}$ <sup>17</sup>). It is considered that the polymer decomposition by depropagation is restricted by small  $G$  (scission); random chain scission then occurs more dominantly than depropagation even to high temperatures, so that the polymer decomposition is controlled by the diffusion of active species below  $120^\circ\text{C}$ .

#### *Polymers of Chlorinated and Fluorinated Methacrylates*

Polymers of chlorinated and fluorinated methacrylates, as a whole, show lower durability for all etching systems than their unsubstituted polymethacrylates. The exact durability depends on the halogen substituent and the etching gas.

Chlorinated and fluorinated polymethacrylates have remarkably low durabilities for plasma etching and  $\text{CCl}_4$ -RSE. Chlorinated polymethacrylates give very high etching rates for plasma ashing, even when aromatic groups are present. It has been reported that the chlorinated crosslinking-type polymers give also high etching rates for plasma ashing.<sup>18</sup> Fluorinated polymethacrylates show somewhat low etching rates for plasma ashing. The order of durability for each etching system is consequently different among the nonhalogenated, chlorinated, and fluorinated methacrylates.



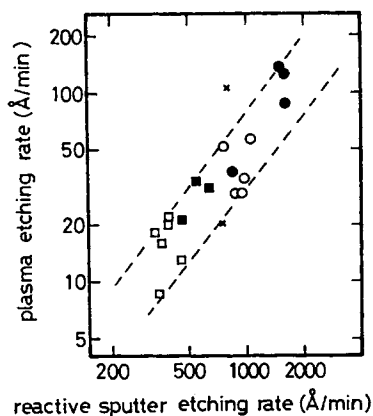


Fig. 5. The correlation between plasma etching rates and reactive sputter etching rates of positive resists for the same etching gas ( $\text{CF}_4 + 5\% \text{O}_2$ ): (O) polymers of alkyl methacrylate; (●) polymers of halogenated alkyl methacrylate; (□) polymers of aromatic methacrylate and  $\text{P}\alpha\text{MeSt}$ ; (■) polymers of halogenated aromatic methacrylate; (X) nonmethacrylate polymers.

The reason for these results cannot be explained clearly. Resist decomposition must occur, at first, by the interaction between a particular atom in the resist molecule and the excited species such as radicals and atomic oxygen produced in the plasma. The interaction energy which exerts the influence upon decomposition rates consists of several components, in which the electrostatic energy and the charge transfer energy contribute dominantly to ionic and radical

TABLE V  
Dry Etching Durabilities of Polymers of Chlorinated and Fluorinated Methacrylate<sup>a</sup>

Sample	Resist etching rate, Å/min			
	Plasma etching	Plasma ashing	$\text{CF}_4$ -reactive sputter etching	$\text{CCl}_4$ -Reactive sputter etching
$\text{PCl}_3\text{EtMA}$	130 (2.5)	2200 (6.9)	860 (1.1)	2400 (1.4)
$\text{PF}_3\text{EtMA}$	130 (2.5)	270 (0.8)	1600 (2.1)	3500 (2.1)
FPM	38 (0.8)	240 (0.8)	850 (1.1)	3500 (2.1)
FBM	140 (2.7)	190 (0.6)	1500 (2.0)	4700 (2.8)
$\text{PFPhMA}$	21 (0.4)	170 (0.5)	460 (0.6)	1500 (0.9)
$\text{PCl}_3\text{PhMA}$	44 (0.8)	1100 (3.4)	540 (0.7)	1800 (1.1)
$\text{PCF}_3\text{PhMA}$	31 (0.6)	160 (0.5)	640 (0.8)	1800 (1.1)

<sup>a</sup> Values in parentheses are the etching rate ratios of each resist to PMMA in each etching system.

TABLE VI  
Dry Etching Durabilities of Nonmethacrylate Polymers<sup>a</sup>

Sample	Resist etching rate, Å/min			
	Plasma etching	Plasma ashing	$\text{CF}_4$ -Reactive sputter etching	$\text{CCl}_4$ -Reactive sputter etching
PMIPK	20 (0.4)	470 (1.5)	750 (1.0)	1400 (0.9)
$\text{PMe}_2\text{IA}$	110 (2.1)	240 (0.8)	800 (1.1)	2200 (1.3)
PBS	3500 (67.0)	8000 (25)		4700 (2.8)

<sup>a</sup> Values in parentheses are the etching rate ratios of each resist to PMMA in each etching system.

reactions, respectively.<sup>19</sup> The resist decomposition in the plasma which must proceed by radical reactions, therefore, is mainly governed by the charge transfer energy from active species to the resist atom, and vice versa. The charge transfer energy could vary with the kind of active species and the electronic state of the resist atom attacked by the active species. As a result, halogenated polymethacrylates should have different durabilities with regard to the kind of etching gas used.

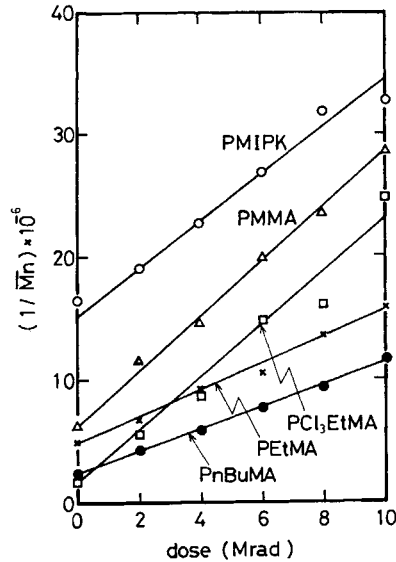


Fig. 6. Determination of  $G$  value for scission from  $1/\bar{M}_n$  vs. dosage of positive resists.

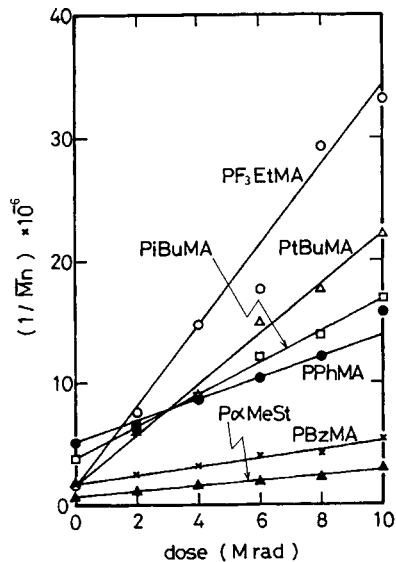


Fig. 7. Determination of  $G$  value for scission from  $1/\bar{M}_n$  vs. dosage of positive resists.

Typical Arrhenius plots of halogenated polymethacrylates are shown in Fig. 3. All activation energies of etching rates exhibit almost the same value (4.4 kcal/mol) in the linear region, which is also equal to that of PMMA. This suggests that the etching rates are controlled similarly by the diffusion of active species. Noteworthy in Fig. 3 is that the bent points of the Arrhenius plots are different from those of the corresponding nonsubstituted polymethacrylates, and those are independent of  $T_g$  ( $T_g$  for FBM, 50°C<sup>8</sup>; for  $\text{PCl}_3\text{EtMA}$ , 138°C<sup>20</sup>; for  $\text{PCl}_3\text{PhMA}$ , 181°C). The reason could depend on the larger  $G(\text{scission})$  values than those of the corresponding nonsubstituted polymethacrylates.

### Nonmethacrylate Polymers

PBS<sup>10</sup> and PMIPK<sup>21</sup> are well-known positive resists. It has been reported that PBS has a low dry etching durability because chain scission is accompanied by extensive depropagation of the radical chain end.<sup>10</sup> This is confirmed by the results in Table VI. The activation energy of 14.5 kcal/mol for PBS etching rates calculated from Fig. 4 suggests that chemical reaction, i.e., the decomposition by depropagation, controls the etching rates because the PBS decomposition rates are considerably faster than the diffusion rates of exited species. The etching rates of  $\text{PMe}_2\text{IA}$ , on the other hand, show a relatively small activation energy (7.8 kcal/mol) even at high etching temperatures. This indicates that  $\text{PMe}_2\text{IA}$  has little tendency to decompose by depropagation.

PMIPK has durabilities similar to those of PMMA, but the durability for plasma etching is remarkably high at low temperature, as shown in Fig. 4. It is considered that the durability of positive resists depends more strongly on their aromatic groups and substituted halogens than on the structure of the polymer skeleton.

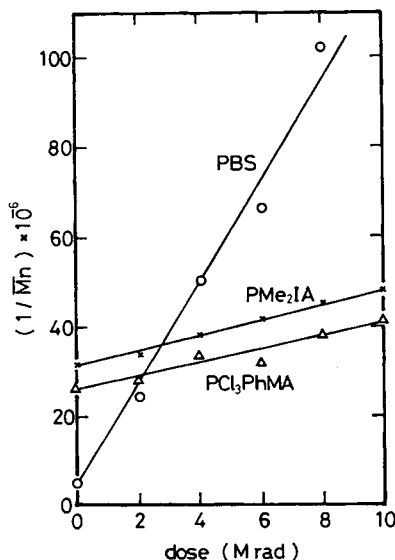


Fig. 8. Determination of  $G$  value for scission from  $1/\bar{M}_n$  vs. dosage of positive resists.

### Contribution of Sputtering Effect on Resist Durability

Figure 5 shows the relationship of resist durabilities between plasma etching and  $\text{CF}_4$ -RSE using the same etching gas. Both etching rates show a good correlation, as shown by the dotted lines. The etching temperature for  $\text{CF}_4$ -RSE was approximately room temperature because the flat-bed electrode where the samples were placed was cooled by tap water. The temperature rise is not considerable because the etching time was less than 10 min. It is therefore considered that decomposition by depropagation could not occur easily because of low etching temperature, and resist decompositions in both etching systems are almost the same, i.e., decomposition by random chain scission. The most important thing to note is that the etching rates for  $\text{CF}_4$ -RSE are about one order of magnitude over that for plasma etching. This result must suggest that positive resists are very vulnerable to such sputtering effects. However, these differences in etching rates are not necessarily due only to the sputtering effect because other etching conditions such as etching pressure and rf power were nonidentical.

The negative resists such as CMS and poly(glycidyl methacrylate)<sup>22</sup> show almost the same behavior to the sputtering effect. Thus, in generally, organic polymers and positive resists are similarly affected by the sputtering effect.

Figure 5 further shows that almost all halogenated polymethacrylates exist near the left dotted line, namely, they have relatively low durability for plasma etching which progresses by chemical reactions. Nonmethacrylate polymers exist beyond the dotted lines.

### Correlation Between Dry Etching Durability and $G$ Value for Scission

Figures 6, 7, and 8 show the relations between inverse number-average molecular weight and  $\gamma$ -radiation dosage for positive resists. Polymers of halogenated methacrylate such as  $\text{PCl}_3\text{EtMA}$ ,  $\text{PF}_3\text{EtMA}$ , and  $\text{PCl}_3\text{PhMA}$  gave relatively large deviations from the linear relationships of  $1/\bar{M}_n$  vs. radiation dosage. This may be due to the very small amount of oxygen. Table VII shows  $G$  (scission) calculated from Figures 6, 7, and 8 compared with values available in the literature. Small differences between these data and literature values could be

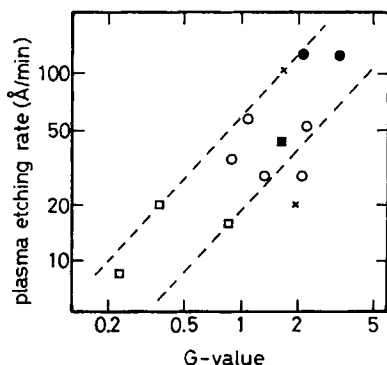


Fig. 9. Correlation between plasma etching rates and  $G$  values for scission of positive resists: (O) polymers of alkyl methacrylate; (●) polymers of halogenated alkyl methacrylate; (□) polymers of aromatic methacrylate and  $\text{P}\alpha\text{MeSt}$ ; (■) polymers of halogenated aromatic methacrylate; (×) nonmethacrylate polymers.

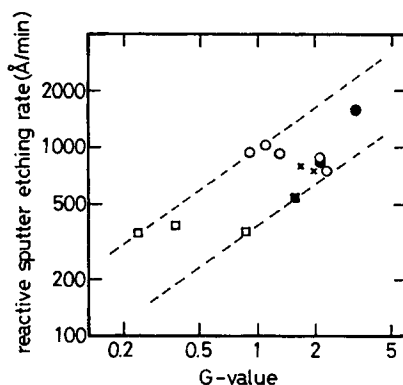


Fig. 10. Correlation between reactive sputter etching rates and  $G$  values for scission of positive resists; (O) polymers of alkyl methacrylate; (●) polymers of halogenated alkyl methacrylate; (□) polymers of aromatic methacrylate and  $P\alpha$ MeSt; (■) polymers of halogenated aromatic methacrylate; (×) nonmethacrylate polymers.

TABLE VII  
 $G$  Values for Scission of Positive Resists from  $\gamma$ -Ray Exposure

Sample	$G$ (scission)	$G$ (scission) literature values
PMMA	2.23	1.87, <sup>7</sup> 1.32 <sup>23</sup>
PEtMA	1.09	1.34 <sup>24</sup>
PnBuMA	0.90	0.69 <sup>24</sup>
PiBuMA	1.33	
PtBuMA	2.03	2.3 <sup>25</sup>
PF <sub>3</sub> EtMA	3.28	
PCl <sub>3</sub> EtMA	2.14	
PPhMA	0.86	0.44 <sup>26</sup>
PCl <sub>3</sub> PhMA	1.56	
PBzMA	0.37	0.14 <sup>26</sup>
PMIPK	1.95	
$P\alpha$ MeSt	0.23	0.25 <sup>27</sup>
PMe <sub>2</sub> IA	1.68	
PBS	12.06	11 <sup>28</sup>

due to the differences of the experimental conditions. Polymers of aromatic methacrylates and  $P\alpha$ MeSt give small  $G$ (scission) values, less than 1.0. Those low values must be attributed to the protective effect described above.

Figures 9 and 10 show the relation between  $G$ (scission) and dry etching rate. They demonstrate rough correlations, so large dispersions are obtained. The dispersions could be attributed to the differences of resist decomposition mechanism between dry etching and  $\gamma$ -irradiation.

The important thing to note therefore is, that the more useful positive resist for the dry process must exist at the right of the bottom in the figures, because the high  $G$ (scission) means high sensitivity and the low etching rate, high durability.

The author is grateful to Dr. S. Sugawara and J. Shimada for their helpful discussion.

## References

1. J. W. Coburn and H. F. Winters, *J. Vac. Sci. Technol.*, **16**, 391 (1979).
2. H. W. Lehmann and R. Widmer, *J. Vac. Sci. Technol.*, **17**, 1177 (1980).
3. S. Imamura, *J. Electrochem. Soc.*, **126**, 1628 (1979).
4. S. Sugawara, O. Kogure, K. Harada, M. Kakuchi, K. Sukegawa, S. Imamura, and K. Miyoshi, 157th Meeting of Electrochem. Soc., St. Louis, Abstract No. 267, 1980.
5. K. Harada, *J. Appl. Polym. Sci.*, **26**, 1961 (1981).
6. M. J. Bowden and L. F. Thompson, *Solid State Technol.*, **72** (1979).
7. E. Gipstein, A. C. Ouano, D. E. Johnson, and O. U. Need III, *IBM J. Res. Develop.*, **143** (1977).
8. M. Kakuchi, S. Sugawara, K. Murase, and K. Matsuyama, *J. Electrochem. Soc.*, **124**, 1648 (1977).
9. K. Murase, M. Kakuchi, and S. Sugawara, in *Proc. Int. Conf. Microlithography, Paris, 1977*, pp. 261-269.
10. M. J. Bowden and L. F. Thompson, *J. Appl. Polym. Sci.*, **17**, 3211 (1973).
11. K. B. Baucom and G. B. Butler, *J. Macromol. Sci. Chem.*, **A8(7)**, (1974).
12. J. L. Vossen, *J. Electrochem. Soc.*, **126(2)**, 319 (1979).
13. L. F. Thompson, *Solid State Technol.*, **41** (1974).
14. J. A. Shetter, *J. Polym. Sci.*, **B1**, 209 (1963).
15. S. Krause, J. J. Gormley, N. Roman, J. A. Shetter, and W. H. Watanabe, *J. Polym. Sci.*, **A3**, 3573 (1965).
16. M. Koike and A. Danno, *J. Phys. Soc. Jpn.*, **15**, 1501 (1960).
17. W. G. Baeb, *J. Polym. Sci.*, **37**, 515 (1959).
18. G. Taylor and T. Wolf, *Photopolymers, Principles, Process and Materials*, Kodak Seminar, Ellenville, Oct. 10-12, 1979, p. 174.
19. S. Nagase and K. Morokuma, *J. Am. Chem. Soc.*, **100**, 1666 (1978).
20. T. Tada, *J. Electrochem. Soc.*, **126**, 1635 (1979).
21. A. W. Levine, M. Kaplan, and E. S. Poliniak, *Polym. Eng. Sci.*, **14(7)**, 518 (1974).
22. T. Hirai, Y. Hatano, and S. Nonogaki, *J. Electrochem. Soc.*, **118**, 669 (1971).
23. A. C. Ouano, D. E. Johnson, B. Dawson, and L. A. Pederson, *J. Polym. Sci.*, **14**, 701 (1976).
24. A. R. Shulz, *J. Polym. Sci.*, **35**, 369 (1959).
25. A. R. Shulz, P. I. Roth, and G. B. Rathman, *J. Polym. Sci.*, **22**, 495 (1956).
26. R. K. Graham, *J. Polym. Sci.*, **37**, 441 (1959).
27. A. M. Kotliar, *J. Appl. Polym. Sci.*, **2**, 134 (1959).
28. J. R. Brown and J. H. O'Donnell, *Macromolecules*, **5**, 109 (1972).

Received January 1, 1981

Accepted March 17, 1981