Synthesis and Characterization of Novel Copolymers with the Trimethylsilyl Group for Deep-UV Photoresists

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ABSTRACT: *N*-(4-Acetoxyphenyl) maleimide (APMI) and three kinds of comonomers bearing a trimethylsilyl group were copolymerized at 60°C in the presence of azobisisobutyronitrile (AIBN) as an initiator in 1,4-dioxane to obtain the three IP, IIP, and IIIP copolymers. These copolymers were removed from the acetoxy group in a transesterification process into new IVP, VP, and VIP copolymers with a pendant hydroxyl group. Two modified processes were adopted to prepare photoresists using these copolymers. The first process involved mixing the dissolution inhibitor, *o*-nitrobenzyl cholate, with the new copolymers. Second, *o*-nitrobenzyl cholate was introduced into the copolymers using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethylformamide (DMF). The cyclic maleimide structure is responsible for the high thermal stability of these copolymers. After irradiation using deep–UV light and development with aqueous Na_2CO_3 (0.01 wt %), the developed patterns showed positive images and exhibited good adhesion to the silicon wafer without using any adhesion promoter. The resolution of these resists was at least 0.8 μm and an oxygen-plasma etching rate was 1/5.3 to that of hard-baked HPR-204. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2791–2798, 2002; DOI 10.1002/app.10255

Key words: trimethyl group; deep-UV photoresist; *o*-nitrobenzyl cholate; oxygen-plasma etching

INTRODUCTION

It is well known that deep-UV lithography employing KrF excimer lasers (248 nm) has emerged as a major technology for ULSI fabrication.[1,2]

One of the primary considerations is to attain high resistance in the photoresist polymers against plasma etching. For obtaining high-resolution patterns, a very thin photoresist film must be used. Therefore, the photoresist needs high etching resistance to oxygen–reactive ion etching (RIE).[3–5] However, there are two steps in the lithographic processes: soft baking and hard baking.[6] The photoresist film should possess good thermal stability to keep the patterns complete during the soft- and hard-baking processes. For these reasons, the photoresist should have high resolution, high sensitivity, high etching resistance, good thermal stability, and high adhesion. These characteristics allow photoresists to be used in the top-imaging layer in a bilayer resist process.

Our laboratory has developed near-UV photoresists using diazonaphthoquinone sulfonate (DNS) as a dissolution inhibitor.[7–10] Deep-UV photoresists were made using photosensitive co-

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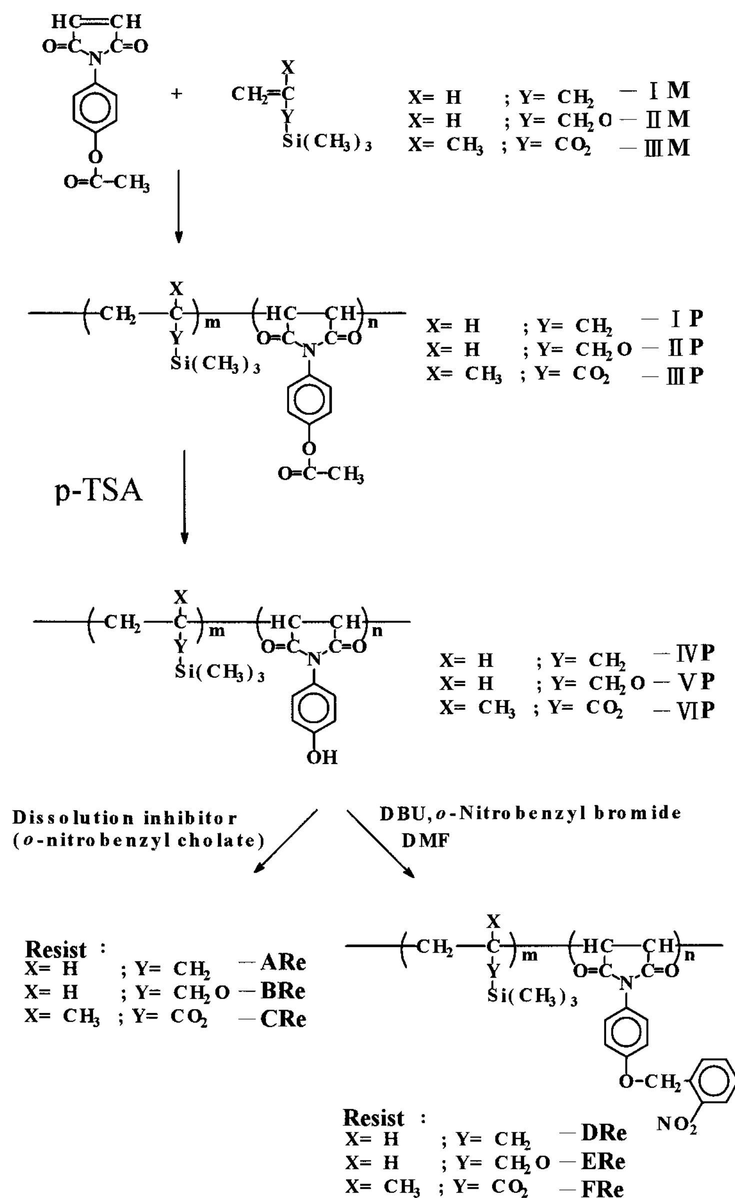


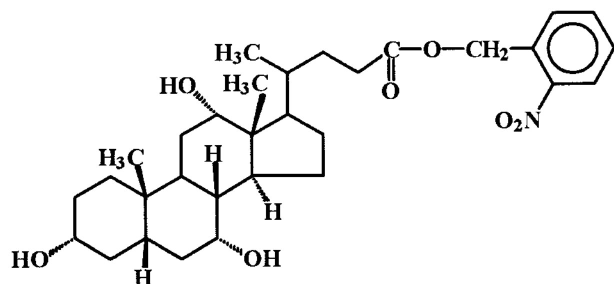
Scheme 1

polymers with the *p*-nitrobenzyl group.[11] The former contains the silyl group with the *o*-nitrobenzyl cholate as a dissolution inhibitor.[12–14] These photoresists show excellent thermal properties and outstanding oxygen-RIE resistance. This study discusses the free-radical copolymerization of N-substituted maleimides (RMI)[15–19] and comonomers containing the trimethylsilyl group. Incidentally, RMI has been very helpful in improving the thermal stability of common vinyl polymers.[20]

EXPERIMENTAL

Laboratory-grade reagents were used without further purification. Among these reagents were maleic anhydride, *p*-aminophenol, sodium acetate, *p*-toluenesulfonic acid, and *o*-nitrobenzyl bromide. Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. Allyltrimethylsilane (I M), allyloxytrimethylsilane (II M), and trimethylsilyl methacrylate (III M) were purified by distillation under reduced pressure. Or-

ganic solvents were distilled after dehydration with calcium hydride. *o*-Nitrobenzyl cholate was prepared using a known synthetic technique.[21,22]



o-Nitrobenzyl cholate

Preparation of Monomers and Copolymers

N-(4-Aceyoxyphenyl) maleimide (APMI) was synthesized as described.[23] The synthesis of the copolymers and preparation of the photoresists was carried out as shown in **Scheme 1.**

Under a nitrogen atmosphere, into a 50-mL polymerization ampoule charged was I M (1.14 g, 0.01 mol), APMI (2.31 g, 0.01 mol), and AIBN (0.0164 g, 0.1 mmol) in 1,4-dioxane (20 mL). The polymerization mixture was then degassed using a freeze–thaw technique and sealed. After copolymerizations at 60°C for 24 h, the copolymer was isolated by precipitation into methanol and further purified by redissolving in 1,4-dioxane and reprecipitating twice into methanol. After drying under vacuum at 60°C for 24 h, the copolymer (IP) of 2.18 g (63.2 wt %) was obtained. Then a 2.00-g sample of IP and 100 mL of acetone were placed into a flask equipped with a condenser. When the copolymer had dissolved, 20 mL of methanol, 20 mL of acetone, and 1.0 g of *p*-toluenesulfonic acid were added. The resulting solution was refluxed for about 2 h and then acetone and methyl acetate were slowly distilled off. The remaining 50 mL solution was poured into methanol. After drying, IVP copolymer was obtained (1.48 g, 74 wt %). Viscosity was measured in dimethylsulfoxide (DMSO) at 30°C and gave $[\eta]$ = 0.26, IR (KBr), 1700, 1770 cm^{-1} (C=O), 1250 cm^{-1} (C—Si), 3200–3600 cm^{-1} (—OH), ^{1}H-NMR (DMSO-d_6), 9.71 δ (phenol groups), 6.77–6.94 δ (aromatic), −0.07 δ (Me—Si). The other copolymers were synthesized in the same way as above.

Synthesis of Poly(allyltrimethylsilane-*co*-*N*-(4-nitrobenzyl-hydroxyphenyl) maleimide (DRe)

A 100-mL round-bottom flask was charged with IVP (1.0 g) in DMF (10 mL). After the polymer had dissolved, a suitable amount of DMF was added and DBU (0.36 g) and *o*-nitrobenzyl bromide (0.5 g) were added dropwise. The amounts of DBU and *o*-nitrobenzyl bromide corresponded to an equal molecular number of the hydroxyl group content of the copolymer, which could be calculated from elemental analyses, based on the N

Table I Polymerization Conditions and Results

Code	M_1 (mol)	M_2 (mol)	T (°C)	Time (h)	AIBN (mmol)	Yield (wt %)	$[\eta]$ (dL/g)
IP	APMI (0.01)	IM (0.01)	60	24	0.1	63.2	0.24
IIP	APMI (0.01)	IIM (0.01)	60	24	0.1	61.8	0.28
IIIP	APMI (0.01)	IIIM (0.01)	60	24	0.1	65.6	0.33

Code	Copolymer (g)	p-Toluenesulfonic acid [g (mmol)]	T (°C)	Time (h)	Yield (wt %)	$[\eta]$ (dL/g)
IVP	**IP** (2)	1 (5.8)	Reflux	2	74	0.26
VP	**IIP** (2)	1 (5.8)	Reflux	2	81	0.28
VIP	**IIIP** (2)	1 (5.8)	Reflux	2	76	0.34

Code	Copolymer	DBU [g (mmol)]	o-Nitrobenzyl Bromide g (mmol)	T (°C)	Time (h)	Yield (wt %)	$[\eta]$ (dL/g)
DRe	**IVP** (1)	0.51 (3.35)	0.73 (3.4)	30	3	82	0.48
ERe	**VP** (1)	0.48 (3.18)	0.69 (3.2)	30	3	78	0.43
FRe	**VIP** (1)	0.45 (2.97)	0.65 (3.0)	30	3	79	0.61

atom. The reaction was carried out at 30°C for 3 h, followed by neutralization with acetic acid and precipitation into water. The resulting polymer was purified by reprecipitation twice from tetrahydrofuran (THF) into *n*-hexane and dried at 60°C in a vacuum oven for 24 h. The DRe polymer was obtained at an 82 wt % yield. Viscosity was measured in DMSO at 30°C and gave $[\eta] = 0.48$, IR (KBr), 1700, 1770 cm^{-1} (C═O), 1250 cm^{-1} (C—Si), ^{1}H-NMR (DMSO-d_6), 6.82–7.51 δ (aromatic), 7.7–8.31 δ (aromatic protons of *o*-nitrobenzyl cholate), −0.07 δ (*t*-Me–Si). The synthesis of the ERe and FRe polymers was the same as above.

Photoresist Processing

Photoresist solutions were prepared using the following two processes. The first involved preparing the resist solutions separately by dissolving 7.5 wt % of the copolymers (IVP, VP, and VIP) in THF and relatively to the copolymer 20 wt % of *o*-nitrobenzyl cholate dissolution inhibitor. The second involved preparing the photoresist solutions by dissolving 7.5 wt % of the photopolymer (DRe, ERe, and FRe) in THF. The solutions were filtered through a 0.25 μm Millipore filter (Millipore Corp., Bedford, MA) before spin-coating on silicon wafers. The compositions of the photoresists are listed as follows:

	Content (wt %)		
Resist Code	THF (mL)	Copolymer	*o*-Nitrobenzyl Cholate[a]
ARe	5	**IVP** (7.5)	20
BRe	5	**VP** (7.5)	20
CRe	5	**VIP** (7.5)	20
DRe	5	**Dre** (7.5)	—
ERe	5	**Ere** (7.5)	—
FRe	5	**Fre** (7.5)	—

[a] Relative to copolymers.

Photoresist films were prepared by spin-coating resist solutions onto 4-in. silicon wafers using a conventional spinner. Wafers were prebaked in a conventional oven at 90°C for 3 min. Film thickness was measured with a stylus instrument (Alpha Step 200; NJ). Deep-UV exposure was carried out using the Hg–Xe lamp with filter (Oriel, Stratford, CT) and the intensity of the light source was determined with an irradiation tester

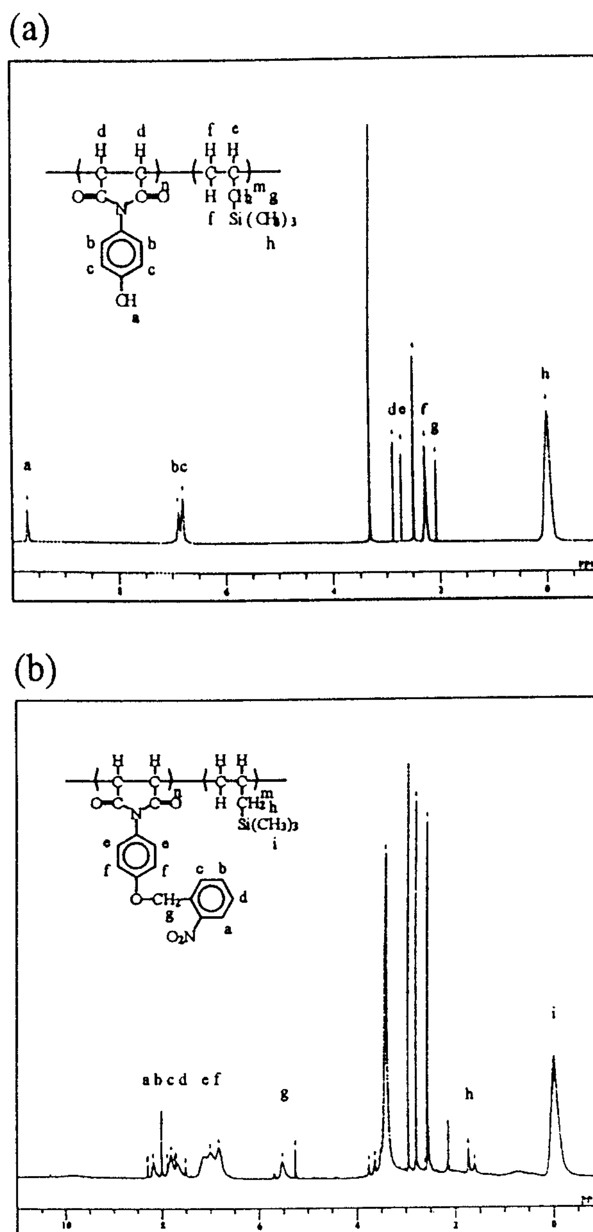


Figure 1 ^{1}H-NMR spectra of **IVP** (a) and **DRe** (b).

(UIT-100; Ushio, Tokyo, Japan). The exposure was carried out with a contact technique using a Toppan resolution mask as a photomask. The exposed films were postbaked in a conventional oven at 130°C for 3 min. After baking, the wafers were soaked in 0.01 wt % of Na_2CO_3 aqueous solution for 20 s before rinsing with water for 10 s.

Measurement

Fourier transform infrared (FTIR) spectra were obtained on a Jasco Model FT/IR 7000 instrument

Table II Elemental Analysis Results for Copolymer

Copolymer	C	H	N	Composition (m/n)	Si Content (wt %)
IVP					
Found	61.3	6.5	4.65	—	—
Anal.	63.3	6.8	4.65	0.955 : 1	9.0
VP					
Found	60.0	6.5	4.60	—	—
Anal.	60.2	6.5	4.60	0.962 : 1	8.6
VIP					
Found	62.3	6.1	4.2	—	—
Anal.	62.5	6.0	4.2	0.931 : 1	7.8

(Tokyo, Japan). ^{1}H-NMR spectra were recorded on a Bruker AM-400 spectrometer (Bruker Instruments, Billerica, MA) in DMSO-d_6 without tetramethylsilane (TMS). The UV absorption was measured on a Jasco V-530 UV/Vis spectrophotometer using a quartz cell. Elemental analyses were performed using a Perkin–Elmer 2400 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT). Intrinsic viscosities were measured with an Ubbelohde viscometer thermostated at 30°C in DMSO. Thermal analyses were performed on a Perkin–Elmer DSC 7 and thermogravimetric analysis (TGA) instrument (DuPont, Wilmington, DE) 2960-SDT. All experiments were conducted under a constant dry nitrogen flow of 20 mL/min (DSC) or 150 mL/min (TGA) and a heating rate of 20°C/min. Adhesion tests were performed according to ASTM-D3359-95b. Oxygen plasma etching resistance of several polymer films was evaluated by using a Mega Strip 6 (Drytek Inc., Wilmington, DE) at RF level power of 1300 W and a chamber pressure of 0.4 mmHg.

Table III Thermal Properties of Copolymer

Copolymer	T_g [a]	T_d [b]	Char Yield (%)
IVP	202.7	319.8	27.8
VP	210.5	304.5	30.6
VIP	213.1	392.8	32.0
DRe	249.3	306.2	22.3
ERe	223.5	294.7	27.9
FRe	250.2	285.2	22.7

[a] From the DSC heating scan, heating rate of 20°C/min in N_2.
[b] Temperature at which 10% weight loss recorded by thermogravimetry at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Preparation and Characterization of Copolymers

Copolymers (IP, IIP, IIIP) and photoresist use copolymers (IVP, VP, VIP) were synthesized and the conditions and results are shown in Table I. Because the copolymers IIP, IIIP, VP, and VIP contain the —O—Si— group, it was considered easy to hydrolyze and to cleave to the —OH group. However, in the copolymerization reagents and solvent were carefully dried and also copolymerized in an ampoule. There was no cleavage in the trimethyl group after copolymerization. The IR absorption band attributed to the C—Si structure appearing at 1250 cm^{-1} also confirmed this. The ^{1}H-NMR spectra of IVP, VP, and VIP showed

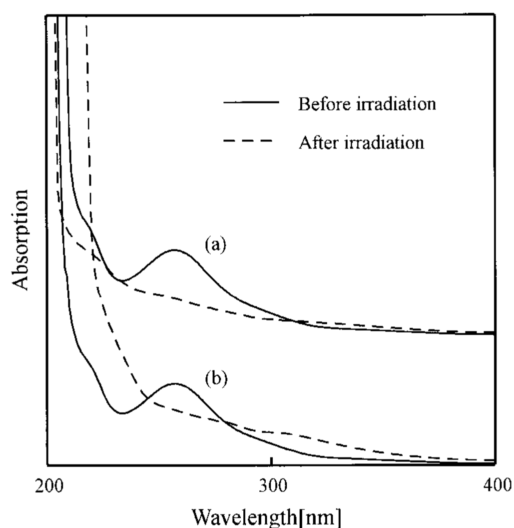


Figure 2 Ultraviolet absorption spectra of **ARe** (a) and **DRe** (b).

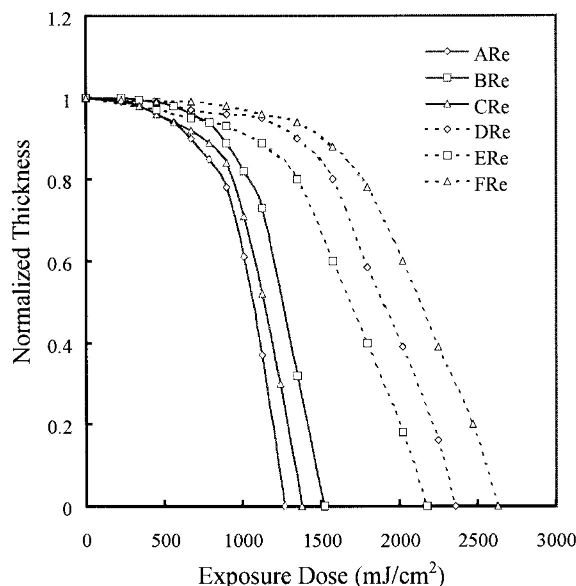


Figure 3 Exposure curves of **ARe–FRe.**

the signal of the trimethylsilyl group at 0–1.0 δ. Figure 1 showed the ^{1}H-NMR spectra of IVP and DRe. The ^{1}H-NMR spectra showed the signal of the trimethylsilyl group at 0–1.0 δ. The spectra peak of ^{1}H-NMR at 9.7 δ is the phenolic OH of IVP and VP. However, the ^{1}H-NMR of phenolic OH of the VIP was at 12.0 δ because it contained external-molecule hydrogen bonding. Phenolic OH absorption was not observed in the copolymers DRe, ERe, and FRe. The absorption bands of the copolymers IVP, VP, and VIP in IR spectra appearing at 3200–3600 cm^{-1} are the absorption of phenolic OH.

Elemental analyses of the IVP, VP, and VIP copolymers, which are summarized in Table II, show that the composition of the copolymers was close to an alternating structure. The electron-rich double bonds of the comonomers tend to undergo alternating copolymerization with electron-poor double bonds of APMI.

The thermal behaviors of the copolymers were evaluated using DSC and TGA. Well-defined melting points (T_m) of these copolymers were not found, probably because of their low crystallinities. The thermal behaviors of the copolymers are listed in Table III. T_g's of polymers are above 200°C and the T_d's of polymers are close to 300°C. The high-temperature stability of the copolymers is attributed to the chain-stiffening effect of the maleimide structure. Moreover, the T_d's (where 10% of the weight was lost) of DRe, ERe, and FRe can be found to be lower than that of IVP, VP, and VIP, which may result from the fact that the photosensitive group is not as stable as phenolic hydroxyl.

Photolysis Reaction of the Photoresist

The change in UV spectra for ARe and DRe is shown in Figure 2. Before irradiation the maximum UV absorption appeared at 256 nm, but after irradiation the peak became smaller. This is characteristic of the photosensitive nitro group. The photosensitive group inhibits the dissolution of the copolymer. After exposure to UV light, the photosensitive group goes through the photochemical reaction for the DRe to form the hydroxyl group, which does not act as a dissolution inhibitor. This phenomenon makes the photoresist show a difference in dissolution in aqueous base before and after exposure.

Characteristics of Photoresists

All of the prepared resists had good adhesion to the silicon wafer without using an adhesion pro-

Table IV Sensitivity, Contrast Ratio, and Oxygen Plasma Etching Rate of the Resists

Code	Sensitivity (mJ/cm^2)	Contrast Ratio	Si Content (wt %)	Etching Rate (Å/min)	Etching Selectivity[a]
ARe	1270	5.6	9.0	79	1 : 5.3
BRe	1520	5.4	8.6	100	1 : 4.2
CRe	1410	4.6	7.8	83	1 : 5.1
DRe	2360	4.5	6.0	127	1 : 3.3
ERe	2180	3.9	5.8	148	1 : 2.8
FRe	2630	4.6	5.4	165	1 : 2.6
Novolac resin (Hunt. HPR-204)	—	—	—	420	—

[a] The etching rate compared to that of HPR-204.

moter. These tests were performed using ASTM-D3359-95b. A 5B level was attained. The exposure–response curves for these two types of resists (Fig. 3) show that the normalized film thickness of the resist decreases with the increase in the dose (i.e., they are positive-type resists). Table IV shows the characteristics of these photoresists. We can see that there is a good contrast present. The radiation response of ARe–CRe is faster than that of DRe–FRe and the sensitivities of the ARe, BRe, and CRe are also higher than those of DRe, ERe, and FRe. Certain factors such as the dissolution parameter and molecular weight do influence sensitivity and contrast. This may arise from the inhibition that occurs when the inhibitor is mixed with IVP, VP, and VIP. In contrast, when the photosensitive group was grafted onto DRe–FRe, the inhibition stemmed from itself. Figure 4 shows the ARe pattern, with the line width of the pattern at 0.8 μm. Because the smallest feature of the mask available was limited to 0.8 μm, we believe that the resolution of these resists should be less than 0.8 μm.

Oxygen Plasma Etching Resistance of Photoresists

The oxygen plasma etching rates for the Si-containing resists relative to that of HPR-204 are shown in Figure 5. The HPR-204 (Novolac resin; Hunt Co., NJ) has a constant etching rate of about

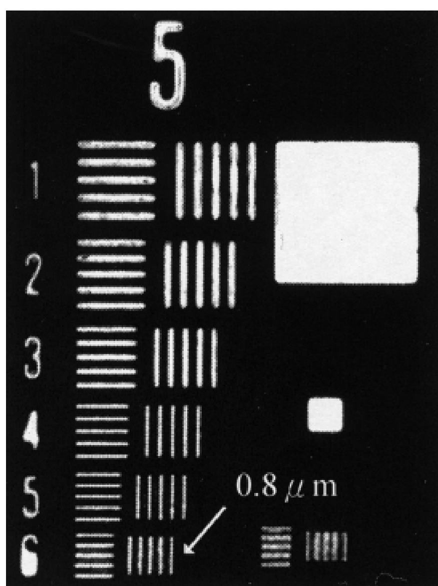


Figure 4 Photograph of the image pattern printed in **ARe.**

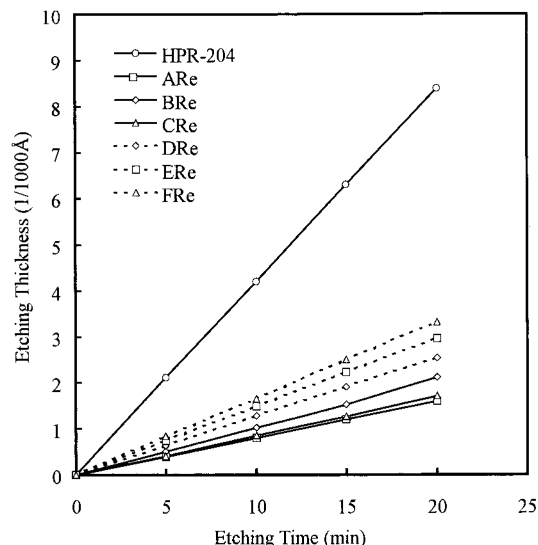


Figure 5 Etching rate of **ARe–FRe.**

420 Å/min. In addition, small amounts of silicon could drastically lower the etching rates of organic polymers. Electron spectroscopy for chemical analysis (ESCA) revealed that the oxygen plasma converted the trimethylsilyl group into silicon oxide or silicon dioxide.[24,25] Because BRe, CRe, ERe, and FRe contain the —O—Si group, it was easy to hydrolyze these resists during the developing process. Therefore, the etching resistances of BRe, CRe, ERe, and FRe were lower than those of ARe and DRe. Consequently, the increase in the silicone content in the photoresists is the most effective method to increase the etching resistance.

CONCLUSIONS

Copolymers IVP, VP, and VIP with the trimethylsilyl group were synthesized through free-radical copolymerization. Six deep-UV photoresists, ARe–FRe, were then prepared. The chain-stiffening effect of the cyclic maleimide group was responsible for high thermal stability. Consequently, the T_g's of these polymers were above 200°C and the T_d's of polymers were close to 300°C. All of the prepared resists had good adhesion to the silicon wafer without using an adhesion promoter. Moreover, these resists showed good resistance to oxygen-plasma etching. The etching selectivity of ARe is 1 : 5.3, compared to that of hard-baked HPR-204. These resists exhib-

ited good contrast value (3.9–5.6) and provided a line/space resolution of 0.8 μm.

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