Synthesis and Characterization of Novel Copolymers of Carboxyphenylmaleimide and Methacrylates with Trimethylsiloxy Groups for Deep-UV Photoresists

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ABSTRACT: *N*-(4-Carboxyphenyl) maleimide (CPMI), with high thermal stability structure, was synthesized from maleic anhydride and *p*-aminobenzoic acid. Free-radical copolymerization of CPMI and three comonomers (**M-1**, **M-2**, and **M-3**) bearing a trimethylsiloxy group was performed at 60°C in the presence of azobisisobutyronitrile as an initiator in 1,4-dioxane. Two different processes were adopted to prepare resists using these copolymers. The first one was to mix the dissolution inhibitor, *o*-nitrobenzyl cholate, into the new copolymers. The second approach was to react the new copolymers with *o*-nitrobenzyl bromide using 1,8-diazabicyclo[5.4.0]undeca-7-ene in dimethylformamide. The cyclic maleimide group was responsible for the high thermal stability. After irradiation by a deep-ultraviolet 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 the use of any adhesion promoter. The resolution of the resists was at least 0.8 μm and the most effective factor for improving the etching selectivity was to increase the silicon content. We found that suitable amounts of silicon (about 14%) can drastically lower the etching rates of organic polymers; that is, an oxygen–plasma etching rate of 1 : 7.92 compared with hard-baked HPR-204. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1032–1037, 2003

Key words: deep-UV; photoresist; lithography; oxygen-plasma etching; copolymerization

INTRODUCTION

Polymers have been increasingly used in many areas of electronics in recent years. One of the main applications for polymers in electronics is as lithographic resists in integrated circuit (IC) fabrication. When the resist is exposed to high-energy radiation such as UV light, electron-beam (EB), or X-rays, certain chemical reactions take place in the exposed area, resulting in a change in its solubility. Utilizing the solubility difference between the exposed and unexposed area, a pattern can be developed using a developer. The main requirements of lithographic resists are high sensitivity, high resolution, high thermal stability, good adhesion to the substrate, and an adequate wet and dry etch resistance.[1,2]

However, it would be very difficult to obtain such fine patterns on wafers with stepped topography using a conventional single-layer process.[3] A bilayer system was suggested to simplify the above process. To obtain high-resolution patterns, a very thin resist film must be used. To achieve this goal, the photoresist needs high etching resistance to oxygen reactive ion etching.[4–6] Electron spectroscopy for chemical analysis (ESCA) reveals that oxygen plasma converts silicon into silicon oxide or silicon dioxide. The resists could be used in the top imaging layer in the bilayer resist process.

Our laboratory has developed near-UV photoresists using diazonaphthoquinone sulfonate as a dissolution inhibitor.[7–10] Deep-UV photoresists, on the other hand, have been made by photosensitive copolymers with the *p*-nitrobenzyl group,[11] and the former contains the silyl group with *o*-nitrobenzyl cholate as a dissolution inhibitor.[12–15]

This study illustrates photoresists made using copolymers containing the trimethylsiloxy group with *o*-nitrobenzyl cholate as a dissolution inhibitor. The resulting photoresists could be used as the top imaging layer in a bilayer resist process and the most effective factor for improving the etching selectivity is to increase the silicon content. We have found that small amounts of silicon (about 14%) can drastically lower the etching rates of organic polymers.

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EXPERIMENTAL

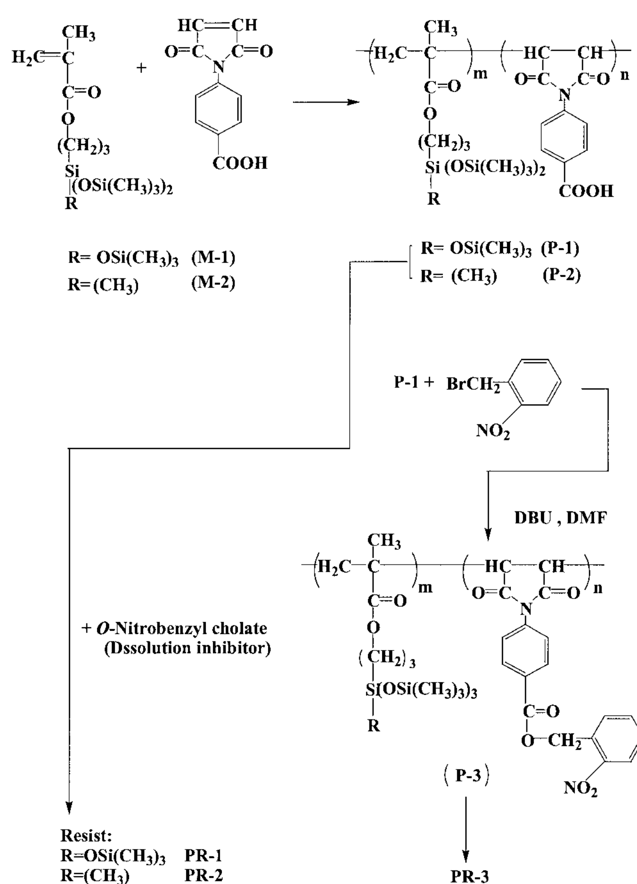
Materials

Laboratory-grade reagents were used without further purification. Among them were maleic anhydride

(Wako Pure Chemical Industries, Osaka, Japan), *p*-aminobenzoic acid (*p*-ABA), and *o*-nitrobenzyl bromide (Lancaster, UK). Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Milwaukee, WI) was recrystallized from methanol before using. 3-(Methacryloyloxy)propyltris(trimethylsiloxy)silane (**M-1**) (Lancaster, UK) and methacryloxypropylbis(trimethylsiloxy)methylsilane (**M-2**) (United Chemical Technologies, Inc., USA) were purified by distillation under reduced pressure. *N*-(4-Carboxyphenyl) maleimide (CPMI) was synthesized by reaction of maleic anhydride with *p*-aminobenzoic acid in the presence of dimethylformamide (DMF) (Tedia, USA) as described. Organic solvents were distilled after dehydration with calcium hydride. *o*-Nitrobenzyl cholate was prepared using a standard synthetic technique.[16,17]

Measurement

FTIR spectra were obtained on a Jasco Model FT/IR 7000 instrument (Jasco, Tokyo, Japan). ^{1}H-NMR spectra were recorded on a Bruker AM-400 spectrometer (Bruker Instruments, Billerica, MA) in DMSO-d_6 (dimethylsulfoxide) (Cambridge Isotope Laboratories, Inc., USA) without tetramethylsilane. We used a Perkin–Elmer 2400 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) to perform elemental analyses. The molecular weight distribution was determined by gel permeation chromatography using a Waters 40 column (Waters Chromatography Division/Millipore, Milford, MA) and THF as solvent. Thermal analyses were performed on a Perkin–Elmer DSC 7 and thermal gravimetric analyzer (TGA) instrument (DuPont, Boston, MA) 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., USA) at RF level power of 1300 W and a chamber pressure of 0.4 mmHg.



Scheme 1 Synthesis and preparation of photoresists.

Copolymerization of poly(3-(methacryloyloxy)propyltris(trimethylsiloxy)silane-*co*-*N*-(4-carboxyphenyl)maleimide) (P-1)

CPMI was synthesized as described.[18] Synthesis of the copolymers and preparation of the photoresists was carried out as shown in Scheme 1.

Under a nitrogen atmosphere, a 50-mL polymerization ampoule was charged with **M-1** (2.114 g, 5 mmol), CPMI (1.085 g, 5 mmol), and AIBN (0.0164 g, 0.1 mmol) in 1,4-dioxane (10 mL). The polymerization

TABLE I
Polymerization Conditions and Yield

Code	Monomer (mmol)	Monomer (mmol)	Solvent (mL)	T (°C)	Time (h)	AIBN (mmol)	Yield (%)
P-1	CPMI[a] 5	M-1 5	1,4-Dioxane (10 mL)	60	24	0.1	74.18
P-2	CPMI 5	M-2 5	1,4-Dioxane (10 mL)	60	24	0.1	76.38

Code	Copolymer (mmol)	DBU (mmol)	*o*-Nitrobenzyl bromide (mmol)	Solvent (mL)	T (°C)	Time (h)	Yield (%)
P-3	P-1 1.7	1.7	1.7	DMF (10 mL)	30	3	71.03

[a] CPMI: *N*-(4-carboxyphenyl)maleimide.

mixture was then degassed with the freeze–thaw technique. The inlet of the ampoule was sealed with the gas–oxygen mixture under a nitrogen atmosphere at low pressure, and then transferred to a thermostated oil bath at 60°C for 24 h. The copolymer was obtained by precipitation into a large amount of dichloromethane. The precipitated polymer was purified twice by reprecipitation for the methanol/dichloromethane then dried in a vacuum at 60°C for 24 h, to obtain the copolymer **P-1** (2.373 g, 74.18 wt %). Viscosity measured in DMF at 30°C gave $[\eta] = 0.32$.

IR (KBr): 1700, 1770 cm^{-1} (C═O), 1250 cm^{-1} (C—Si), 3200–3600 cm^{-1} (–OH), 1065 cm^{-1} (Si—O). ^{1}H-NMR (DMSO-d_6): 7.61–8.03 δ (aromatic protons), 0 δ (*t*-Me—Si).

Copolymerization of poly(methacryloxypropylbis(trimethylsiloxy)-methylsilane-*co*-*N*-(4-carboxyphenyl)maleimide) (P-2)

The copolymer P-2 was synthesized in the same way as for **P-1**.

Synthesis of poly(3-(methacryloyloxy)propyl-tris(trimethylsiloxy)silane-*co*-*N*-(4-(*o*-nitobenzylcarbonate)-phenyl)maleimide) (P-3)

A 100-mL round-bottom flask was charged with copolymer P-1 (1.0 g) in DMF (10 mL). After the polymer had dissolved, a suitable amount of DMF (5 mL) was added, after which 1,8-diazabicyclo[5.4.0]undeca-7-ene (DBU) (Aldrich Chemical Co.) (0.26 g) and *o*-nitrobenzyl bromide (0.35 g) were added drop by drop. The amounts of DBU and *o*-nitrobenzyl bromide corresponded to an equal molecular number of the –COOH group content of the copolymer, which could be calculated by elemental analyses. 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 THF into *n*-hexane and dried at 60°C in a vacuum oven for 24 h. The polymer **P-3** was obtained (1.143 g, 71.03 wt %).

IR (KBr): 1530 and 1350 cm^{-1} (NO_2), 1770 cm^{-1} (C═O), 1250 cm^{-1} (C—Si), 1065 cm^{-1} (Si—O). ^{1}H-NMR (DMSO-d_6): 7.2–7.7 δ (aromatic protons), 7.8–8.3 δ (aromatic protons of *o*-nitrobenzyl cholate), 0 δ (*t*-Me—Si).

Photoresist processing

Resist solutions were prepared by two processes. The first process was to prepare the resist solutions separately by dissolving 7.5 wt % of the copolymers (**P-1** and **P-2**) in THF and 20 wt % (relative to the copolymer) of the *o*-nitrobenzyl cholate dissolution inhibitor. The second process was to prepare separately the resist solutions by dissolving 7.5 wt % of the photopolymer (**P-3**) in THF. The solutions were filtered through a 0.25-μm Millipore filter (Milford, MA) before spin-coating on silicon wafers. The compositions of the prepared photoresists are listed as follows:

Resist code	Content (wt %)		
	THF[a] (g)	Copolymer[b]	*o*-Nitrobenzyl cholate[c]
PR-1	4.44	**P-1** (7.5%)	20%
PR-2	4.44	**P-2** (7.5%)	20%
PR-3	4.44	**P-3** (7.5%)	—

[a] The 5 mL of THF is equal to 4.44 g.
[b] Compared to the solvent.
[c] Relative to copolymers.

Resist films were prepared by spin coating resist solution onto 4-in. silicon wafers using a conventional spinner and were prebaked in a conventional oven at 90°C for 3 min. Film thickness was measured with a stylus instrument (Alpha Step 200). Deep-UV exposure was carried out by using the Hg–Xe lamp-filter combination (Oriel) and the intensity of the light source was determined with an irradiance tester (Ushio, UIT-100). The exposure was carried out by the contact technique using a Toppan resolution mask as a photomask. The exposure 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 60 s before rinsing with water for 10 s.

RESULTS AND DISCUSSION

Copolymer preparation and characterization

Copolymers were synthesized by free-radical copolymerization at 60°C in 1,4-dioxane. The conditions and results are shown in Table I. Because the copolymers (**P-1**, **P-2**, and **P-3**) 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 bands of the copolymers **P-1** and **P-2** in IR spectra appeared at 3200–3600 cm^{-1}. Their wide range came from the absorption of phenolic OH. The band appearing at 1250 cm^{-1} is attributed to the absorption of the C—Si structure. The ^{1}H-NMR spectra of copolymers showed a trimethylsiloxy group at 0 δ, aromatic protons at 7.61–8.03 δ, and –COOH protons at 12.50–13.00 δ.

The polymerization result and elemental analyses of copolymers are summarized in Table II, which shows that the composition of the copolymers was closed to an alternating structure. The Si-containing monomers tend to undergo alternating copolymerization with electron-poor double bonds of CPMI. The thermal behaviors of the copolymers were evaluated by

TABLE II
Polymerization Results and Elemental Analysis Results for Copolymers

Copolymer	C (%)	H (%)	N (%)	Si (%)	m/n	T_d (°C)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	Polydispersity
P-1									
Found	50.91	6.96	2.28	17.15	0.94	348.88	54.46	32.78	1.66
Anal	50.70	7.04	2.19	17.23	—				
P-2									
Found	53.03	6.82	2.53	14.58	0.96	346.12	64.71	42.48	1.52
Anal	52.91	6.87	2.46	14.81	—				
P-3									
Found	51.93	6.11	4.11	14.47	0.78	263.32	66.64	45.33	1.47
Anal	51.16	6.46	3.61	12.08					

means of DSC and TGA. In the DSC curve, no distinct glass-transition temperature (T_g) was observed. Well-defined melting points (T_m) of these copolymers were not found, probably the result of their low crystallinities. The decomposition temperature T_d (where 10% of the weight was lost) of those copolymers was >300°C, meaning that they have good thermal stability in the photoresist process, likely the consequence of the chain-stiffening effect of the maleimide structure.

Characteristics of photoresists

The spin-coating condition has an important effect on the film thickness that affects the characteristics of the resists. The resists' coating thickness curves of **PR-1**, **PR-2**, and **PR-3** are shown in Figure 1. When optimum coating conditions (spin speed is about 2500 rpm for 30 s) are used, coating uniformity in 1- to 2-μm-thick film can be achieved across a 4-in. wafer.

The contents of *o*-nitrobenzyl cholate influence the dissolution rate of exposed and unexposed parts as a dissolution promoter and an inhibitor, respectively. Then, the influence of *o*-nitrobenzyl cholate content on the dissolution rate in the developer of 0.01% Na_2CO_3 solution after exposure was studied (Fig. 2). The exposed part was virtually unchanged at a load of 20 wt % *o*-nitrobenzyl cholate. These results indicate that *o*-nitrobenzyl cholate acts as a dissolution promoter in the exposed part, but does not act as a dissolution inhibitor probably because of a high hydrophobicity of the photoresist in the unexposed part. A 20 wt % loading of *o*-nitrobenzyl cholate is necessary to achieve a good dissolution contrast.

All of the prepared resists had good adhesion to the silicon wafer without using an adhesion promoter. The exposure response curves of 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 III shows the characteristics of photoresists, from which one may see a characteristically good contrast. Besides, the radiation response of **PR-1** or **PR-2** is faster than that of **PR-3**, and the sensitivities of **PR-1** and **PR-2** are also higher than those of **PR-3**. Certain factors such as the dissolution parameter and molecular weight do influ-

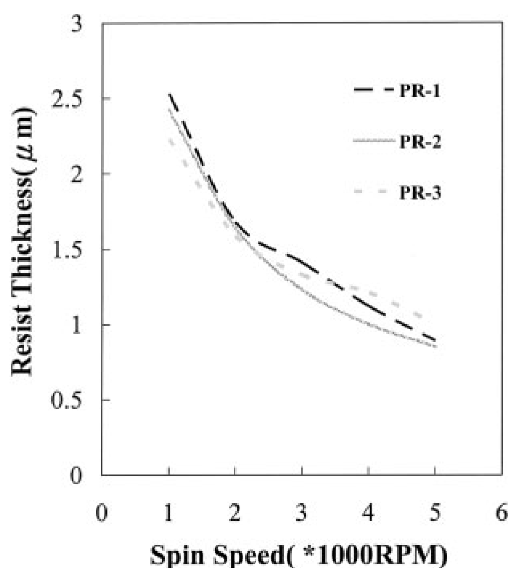


Figure 1 Coating resist thickness versus spin speed.

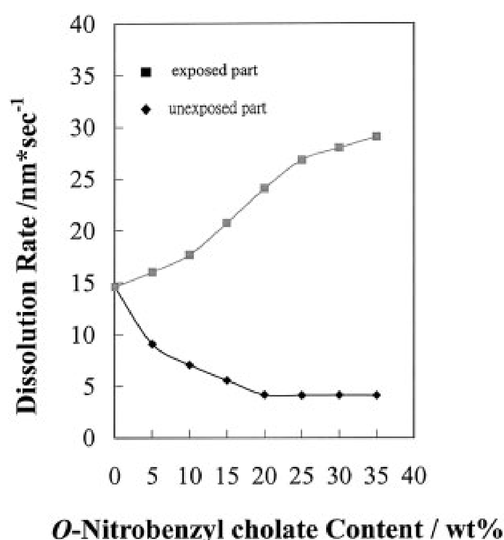


Figure 2 Effect of *o*-nitrobenzyl cholate content of the **P-1** film on the dissolution rate.

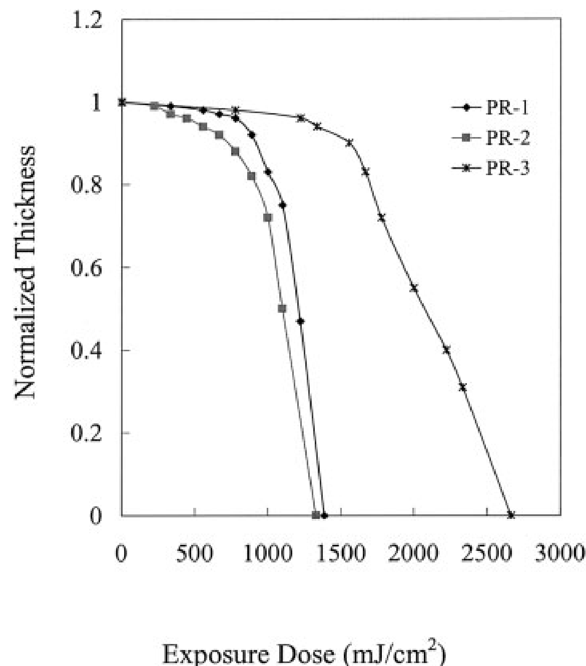


Figure 3 Exposure–response curves of the resists.

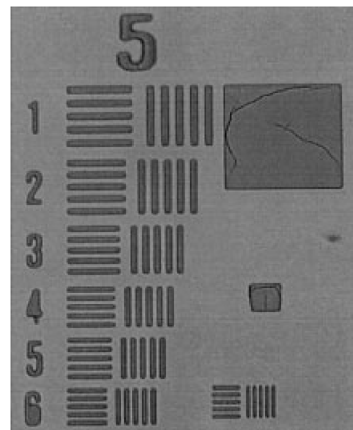


Figure 4 Microphotograph of the image pattern based on **PR-1**.

ence sensitivity and contrast. This may arise from the inhibition that occurs when the inhibitor is mixed with **P-1** and **P-2**. In contrast, when the photosensitive group was grafted onto **P-3**, the inhibition stemmed from itself. Figure 4 shows the pattern of **PR-1**, 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 the resists should be less than 0.8 μm.

Oxygen plasma etching resistance

The oxygen plasma etching rates of the Si-containing resists relative to HPR-204 are shown in Figure 5. The oxygen plasma etching results of the resists were examined and compared with HPR-204, as shown in Table III. The HPR-204 (Hunt Co., Novolac resin) has a constant etching rate of about 420 Å/min. In addition, note the increase in etching selectivity from 5.30 to 7.92 for ARe with a content of 9.00 wt % silicon and **PR-2** with a content of 14.58 wt % silicon. The relationship between the increase in etching selectivity with a content of 17.15 wt % silicon for **PR-1** is not clear. ESCA revealed that the siloxy group in copolymer was converted into silicon oxide or silicon dioxide by the oxidation with the oxygen plasma.[20,21] Therefore, it is concluded that the increase in the silicon content is the most effective factor in the increase of etching resistance.

CONCLUSIONS

Copolymers **P-1** and **P-2** with the siloxy group were synthesized through free-radical copolymerization, after which the deep-UV photoresists **PR-1–PR-3** were prepared by dissolving copolymers. The chain-stiffening effect of the cyclic maleimide group was responsible for high thermal stability. All of the prepared resists had good adhesion to the silicon wafer without using an adhesion promoter. Moreover, resists showed good resistance to oxygen plasma etching, and the etching selectivity of **PR-1** is 1 : 7.92, compared to that of hard-baked HPR-204. The resists had good contrast value (3.7–6.8) and provided a line/space resolution of 0.8 μm.

TABLE III
Characteristics and Oxygen Plasma Etching Results of Photoresists

Code	Sensitivity (mJ/cm^2)	Contrast ratio	Si content (wt %)	Etching rate (Å/min)	Etching selectivity[a]
P-1	1387	6.8	17.15	57	1 : 7.36
P-2	1330	6.7	14.58	53	1 : 7.92
P-3	2664	3.7	12.80	71	1 : 5.91
ARe[b]	1270	5.6	9.00	79	1 : 5.30
Novolac resin (HPR-204)	—	—	—	420	—

[a] The etching rate compared to that of HPR-204.
[b] Ref 19.

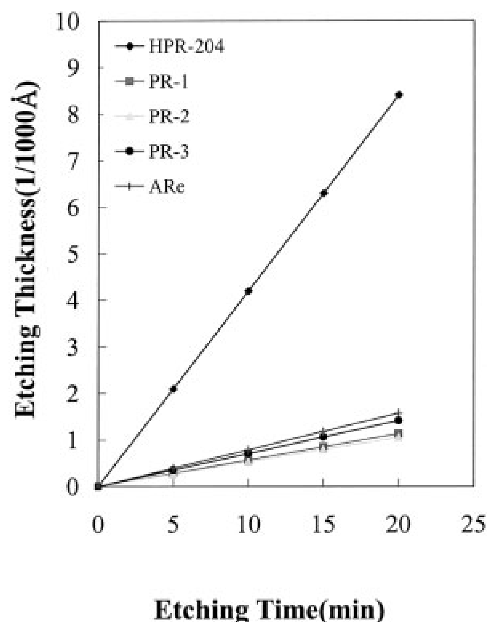


Figure 5 Oxygen plasma etching rates of the resists compared with that of HPR-204.

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