

Preparation and Properties of Si-Containing Copolymer for Near-UV Resist. III. Maleimide/Silylstyrene Copolymer*

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SYNOPSIS

Poly(maleimide-*alt-p*-trimethylsilyl- α -methylstyrene) (α -PMTMMS) and poly(maleimide-*alt-p*-trimethylsilylstyrene) (PMTMSS) were synthesized for positive/negative near-UV resists in the containing of diazonaphthoquinone sulfonate (DNS). The electron-rich styrenic monomers tend to undergo alternating copolymerization with an electron-poor maleimide monomer. The chain-stiffening effects of the maleimide and α -methylstyrene group were responsible for high thermal stabilities. A higher glass transition temperature of 226°C was found in α -PMTMMS. Lithographic positive/negative images were obtained that were stable to temperatures higher than 200°C. Excellent solubility in aqueous base was observed with PMTMSS at 10.3 wt % silicon content and an oxygen-plasma etching rate of 1 : 12 compared to hard-baked HPR-204. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A typical positive photoresist is generally a two-component material consisting of an alkaline soluble polymer that is rendered insoluble in aqueous alkaline solutions through addition of a radiation-sensitive dissolution inhibitor such as diazonaphthoquinone sulfonate (DNS). The most widely used positive photoresist is a novolac resin (condensation polymer of formaldehyde and phenol) with DNS. To date, several advanced IC manufactures require images that are stable to 200°C and even more. The novolac-based resists are unable to perform very well in this range. Thus, some other phenolic polymers¹⁻⁴ have been shown to serve as replacements for conventional novolac-based resists. The general alkaline soluble polymers have carboxylic acids or maleimides as well as phenolic units. For example, poly(*p*-vinylbenzoic acid)⁵ and maleimide/styrene⁶ copolymer have been applied to positive imaging of high-temperature polymers. In addition, maleimide/allyltrimethylsilane copolymer⁷ with DNS for use as the top imaging layer in a bilayer resist process

has attracted considerable interest because of its excellent durability to oxygen-plasma etching. Taylor et al.⁸ reported that small amounts of silicon (about 10 wt %) can drastically lower the oxygen-plasma etching rate of organic polymers. Anyway, the bilayer resist processes appear to be the most practical processing technology to attain high-resolution patterns for future device fabrication.⁹ In this study, for increasing the thermal stability of maleimide/allyltrimethylsilane, the allyltrimethylsilane unit is replaced by silylstyrene (*p*-trimethylsilylstyrene, *p*-trimethylsilyl- α -methylstyrene) in the copolymer structure. We have reported^{10,11} that *N*-(4-hydroxyphenyl)maleimide/*p*-trimethylsilylstyrene (PHTMSS) and *N*-(4-hydroxyphenyl)-maleimide/*p*-trimethylsilyl- α -methylstyrene (α -PHTMMS) were applied as the top imaging layers; their silicon content (about 7 wt %) was not enough to allow etching of bottom hard-baked HPR-204 film without line-width loss. For increasing the silicon content of the copolymer, the *N*-(4-hydroxyphenyl)maleimide unit is replaced by the maleimide group. Consequently, PMTMSS and α -PMTMMS are prepared to act as high thermal stable and oxygen-plasma etching resistant resists in this study.

In our previous papers,^{10,11} PHTMSS was initially used as an alkaline soluble polymer for DNS photochemical reaction and positive images should have

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been obtained. However, negative images were obtained. It was proposed that photocross-linking occurred in the PHTMSS main chain such as the α -carbon position at vinyl group of *p*-trimethylsilylstyrene (TMSS). To prevent cross-linking from occurring, the hydrogen on α -carbon of TMSS would be substituted to the methyl group to prepare *p*-trimethylsilyl- α -methylstyrene (α -TMMS). Thus, α -PHTMMS was prepared, which formed a positive image for DNS photochemical reaction as expected. PMTMSS and α -PMTMMS will show the same result.

EXPERIMENTAL

Materials

Maleimide was laboratory grade and used without further purification. Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. Tetrahydrofuran (THF) was distilled after dehydration with sodium. α -Methylstyrene, styrene, α -methyl-*p*-chlorostyrene, and *p*-chlorostyrene were distilled before use.

Syntheses

Para-trimethylsilyl- α -methylstyrene (α -TMMS) and Para-trimethylsilylstyrene (TMSS)

α -TMMS was synthesized in the similar way as we prepared TMSS.¹⁰

Poly(maleimide-*alt-p*-trimethylsilyl- α -methylstyrene) (α -PMTMMS)

Under a nitrogen atmosphere, a 50 mL polymerization ampule was charged in 0.97 g (0.01 mol) of maleimide, 1.90 g (0.01 mol) of α -TMMS, 15 mL of dry THF, and 0.02 g of AIBN. The ampule was quenched by dry ice-acetone and sealed. Copolymerization was carried out in a 60°C bath for 24 h. The obtained copolymer was isolated by precipitation of the viscous polymerization solution into ether. After drying under vacuum at 60°C for 24 h, 85 wt % of copolymer was obtained. Viscosity, measured in THF at 30°C, gave $[\eta] = 0.58$. GPC analysis in THF gave $M_w = 37,800$; $M_n = 19,300$, and calculated polydispersity = 1.96.

ANAL: Calcd for C₁₆H₂₁NO₂Si (1 : 1 structure): C, 66.90%; H, 7.32%; N, 4.88%.

Found: C, 66.85%; H, 7.34%; N, 4.84%.

The other maleimide copolymers were synthesized in the same way as above.

Photoresist Processing

Resist Preparation

Resist solutions were prepared by dissolving 5 wt % of the prepared copolymer and 3 wt % of benzophenone-tri-diazonaphthoquinone sulfonate (BP-t-DNS) as an alkaline insoluble sensitizer in 92 wt % of THF. The solutions were filtered through a 0.5 μ m Millipore filter.

Spin Coating and Soft Baking

Resists were spin-coated (4000 rpm) on 4 in. silicon wafers to yield a 1.2–1.6 μ m film thickness using a spinner (Silicon Valley Group Inc., Model SVG-8026). The resist films were prebaked in a conventional oven at 50°C for 30 min.

Exposure and Developing

Near UV exposures (350–450 nm) were carried out using a Canon Contact Aligner PLA-501F. After exposure, the wafers were soaked in 5 wt % tetramethylammonium hydroxide (TMAH) (HUNT Co.) for positive images or continuously rinsed in THF or acetone for negative images with an agitation developer (SVG-8132). The film thickness was measured with a TENCO α -step 200 instrument.

Postbaking

The developed patterns were postbaked in a conventional oven at 100–300°C for 30 min.

Measurement of Various Properties

FTIR spectra were obtained on a JASCO Model FT/IR 7000 instrument. Elemental analyses were determined by using a Perkin-Elmer 2400 instrument. The molecular weight and dispersity of the copolymer was measured using Shimadzu Model LC-6A gel permeation chromatography equipped with an RI detector (Shimadzu, RID-6A). The GPC measurement was performed in a polymer/THF solution (about 0.3–0.4 g/100 dL) using two styragel columns, i.e., G1000H and G3000H under the flow rate 1 mL/min at 40°C. The calibration curve was plotted using monodisperse polystyrene (molecular weight: 500–1,260,000). The average molecular weight was calculated on the basis of Shimadzu C-R4A GPC Program V 1.1. Thermal analyses were performed on a DuPont TA-2000 thermal analyzer coupled with a 910 DSC module and a DuPont 951 thermogravimetric analyzer. The adhesion test was performed according to ASTM-D3359-83. Oxygen-

plasma etching resistance of several polymer films were evaluated using a Mega Strip 6 (Drytek Inc.). The quality of image in the resist patterns was evaluated with a Nikon optical microscope.

RESULTS AND DISCUSSION

Preparation of Copolymer

Several maleimide/styrenic monomer copolymers were prepared. The reactive conditions and molecular weight of the copolymers are shown in Table I. The electron-rich α -methylstyrene (*p*-chloro- α -methylstyrene, *p*-silyl- α -methylstyrene) monomer lacks propagation to homopolymerize by radical polymerization, but it can easily copolymerize with an electron-poor maleimide monomer by radical polymerization. An equimolar monomer feed ratio was used to prepare the copolymer. The copolymer was isolated by precipitation of the viscous polymerization solution into ether, not methanol. Because maleimide monomer shows good solubility in methanol (1 : 20), the hot viscous polymerization solution is readily soluble in methanol. On the other hand, polysilylstyrene is easily soluble in ether. For this reason, ether was used not only as the precipitator but also as the purification agent of the silicon-containing copolymer. Figure 1 shows the FTIR spectra of α -PMTMMS and PMTMSS. It shows N—H stretching vibrations of the imide ring at 3240 cm^{-1} ; cyclic imide absorption bands at 1780 , 1150 , and 690 cm^{-1} ; and a characteristic silane absorption peak at 1250 cm^{-1} . Table II shows the structure of the copolymer. α -PMTMMS is predominately alternating

Table I The Preparation of Copolymer^a

Polymer Code	Yield (%)	$[\eta]^b$	\bar{M}_n	\bar{M}_w^c	PI ^d
α -PMTMMS	85	0.58	19,300	37,800	1.96
PMTMSS	92	0.55	18,100	31,000	1.71
α -PMMS	81	0.33	8,500	14,200	1.67
PMS	88	0.43	15,600	29,600	1.89
α -PMCMS	78	0.32	7,600	12,900	1.69
PMCS	86	0.46	18,000	25,500	1.41

^a Copolymerization was carried out with 0.97 g (0.01 mol) of maleimide, 0.01 mol comonomer, and 0.02 g of AIBN in 15 mL of THF at 60°C under nitrogen for 24 h.

^b Intrinsic viscosity was measured in an Ubbelohde viscometer at 30°C .

^c Molecular weight was determined with GPC on the basis of polystyrene.

^d Polydispersity.

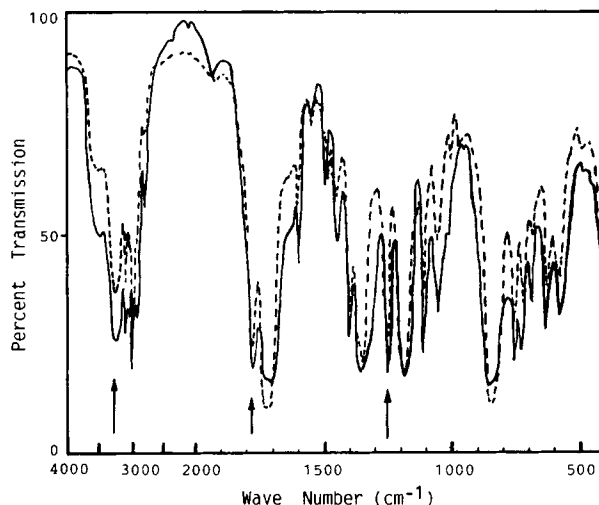


Figure 1 FTIR spectra of (----) α -PMTMMS and PMTMSS (—).

because of the opposite polarity of the double bonds of comonomers. The electron-rich double bond of α -TMMS tends to undergo alternating copolymerization with the electron-poor double bond of maleimide. This classic behavior is well documented for similar systems: maleimides/styrene,⁶ maleimide/allyltrimethylsilane,⁷ *N*-phenylmaleimide/styrene,¹² *N*-(4-hydroxyphenyl)maleimide/styrene,^{1,13} and *N*-(4-hydroxyphenyl)maleimide/TMSS.¹⁰ The other maleimide/styrenic monomer copolymers were also close to 1 : 1 in compositions as determined by elemental analyses as shown in Table III.

Table II The Structure of the Copolymer

Polymer Code	R	X	Z
α -PMTMMS	CH ₃	Si(CH ₃) ₃	H
PMTMSS	H	Si(CH ₃) ₃	H
α -PMMS	CH ₃	H	H
PMS	H	H	H
α -PMCMS	CH ₃	Cl	H
PMCS	H	Cl	H
α -PHTMMS	CH ₃	Si(CH ₃) ₃	Ph—OH
PHTMSS	H	Si(CH ₃) ₃	Ph—OH

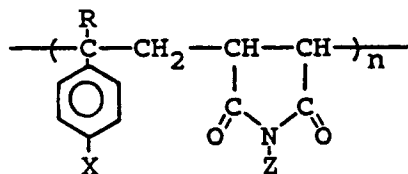


Table III Elemental Analyses of Copolymers^a

Polymer Code	1 : 1 Formula	Calculated (%)			Found (%)		
		C	H	N	C	H	N
α -PMTMMS	C ₁₆ H ₂₁ NO ₂ Si	66.90	7.32	4.88	66.85	7.34	4.84
PMTMSS	C ₁₅ H ₁₉ NO ₂ Si	65.93	6.96	5.13	65.81	6.93	5.12
α -PMMS	C ₁₃ H ₁₃ NO ₂	72.56	6.04	6.51	72.42	6.03	6.56
PMS	C ₁₂ H ₁₁ NO ₂	71.64	5.47	6.96	71.58	5.51	6.93
α -PMCMS	C ₁₃ H ₁₂ NO ₂ Cl	62.52	4.81	5.61	62.45	4.83	5.61
PMCS	C ₁₂ H ₁₀ NO ₂ Cl	61.15	4.25	5.94	61.08	4.27	5.92

^a Copolymerization was carried out with 1 : 1 feed mole ratio.

Polymer Characterization

Because the prepared copolymers are alternating, sufficient alkaline solubilities are obtained at 50% maleimide units. Ohnishi et al.¹⁴ reported that the solubility of novolac resin in a base solution decreased greatly by introducing the trialkylsilyl group. Maleimide/*p*-trimethylsilylstyrene (PMTMSS) copolymer, which is prepared by introducing trimethylsilane into maleimide/styrene (PMS) copolymer, is also readily soluble in an aqueous base such as aqueous sodium hydroxide or TMAH. All the prepared copolymers show excellent solubility in polar solvents such as dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc), and pyridine. They are also soluble in common organic solvents like THF and acetone.

The thermal stability and glass transition temperatures (T_g) of copolymers were evaluated by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC), respectively. Figure 2

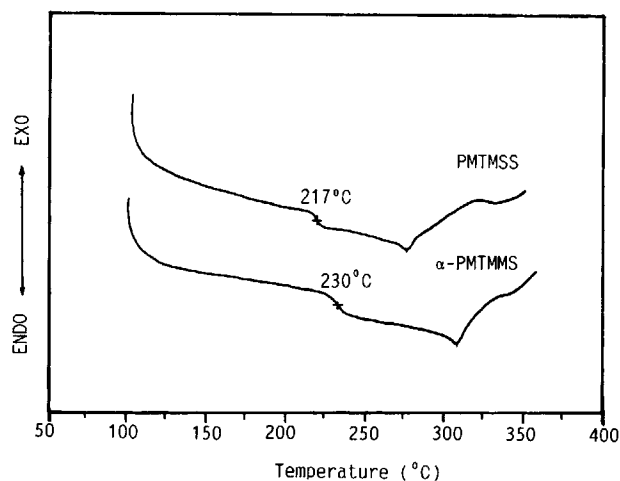


Figure 2 DSC curves of α -PMTMMS and PMTMSS.

shows DSC curves of α -PMTMMS and PMTMSS in nitrogen at a heating rate of 10°C/min. It has been reported¹⁵ that poly(α -methylstyrene) has a T_g of 170°C compared to 100°C for polystyrene. As expected, α -PMTMMS has a higher T_g of 230°C compared to 216°C for PMTMSS. The higher values correspond to the greater thermal stability of the α -methylstyrene unit. Figure 3 presents the typical TGA curves of the polymers in nitrogen at a heating rate of 20°C/min. No copolymers exhibited weight loss below 350°C. From the traces, polystyrene completely decomposed at about 470°C. The other polymers had > 10 wt % remaining even at 600°C. The char yield is due to the chain-stiffening effect of the maleimide monomer.

Lithographic Characteristics

The alkaline soluble polymer was rendered insoluble in aqueous base through the addition of a base-insoluble sensitizer like DNS. Ordinarily, after being

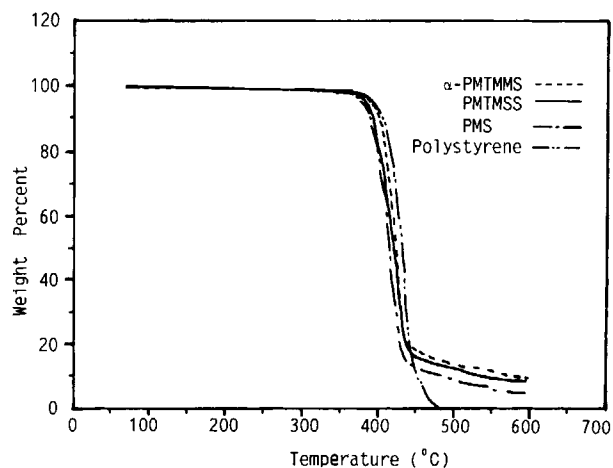


Figure 3 TGA curves of the polymers.

exposed to radiation, the DNS would bring about carbene formation. Through the Wolff rearrangement, ketene was formed and then reacted with water to form a base-soluble indenecarboxylic acid¹⁵ that no longer inhibited dissolution of the polymer in the aqueous base, thereby facilitating development of a positive image, i.e., a typical two-component positive photoresist.

In this experiment, the copolymers were applied as binders for DNS photochemical reaction; positive images should be obtained except for maleimide/TMSS (PMTMSS), which attained a negative image. This unusual phenomenon has also been found in *N*-(4-hydroxyphenyl) maleimide/TMSS (PHTMSS).^{10,11} It was proposed that photocross-linking occurred in the polymer main chain, such as at the α -carbon position at the vinyl group of TMSS. The hydrogen at the α -carbon position will be abstracted and the stable benzylic radical will be yielded at the end. To prevent cross-linking from occurring, the hydrogen at the α -carbon position would be substituted by a methyl group to synthesize α -TMMS. In other words, *N*-(4-hydroxyphenyl) maleimide/ α -TMMS (α -PHTMMS) was prepared that attained a positive image for the DNS photochemical reaction. In this study, maleimide/ α -TMMS (α -PMTMMS) will also form a positive image, as it is designed to do. The exposure response curves of resists are shown in Figure 4, which shows that the normalized film thickness of the α -PMTMMS resist decreases with increase of the dose that is a positive-type resist (sensitivity: 222.6 mJ/cm²). Conversely, the PMTMSS resist is a negative-type resist (sensitivity: 47.7 mJ/cm²). When applied in a single-layer resist system, the prepared silicon-

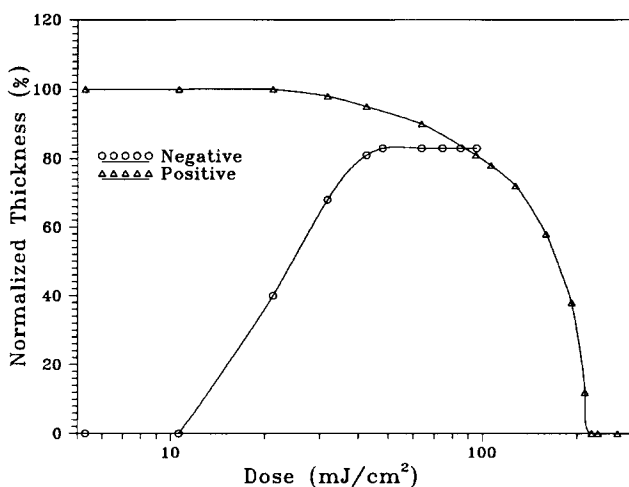
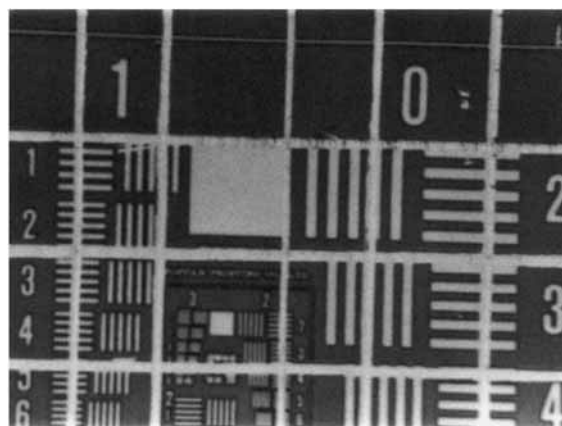
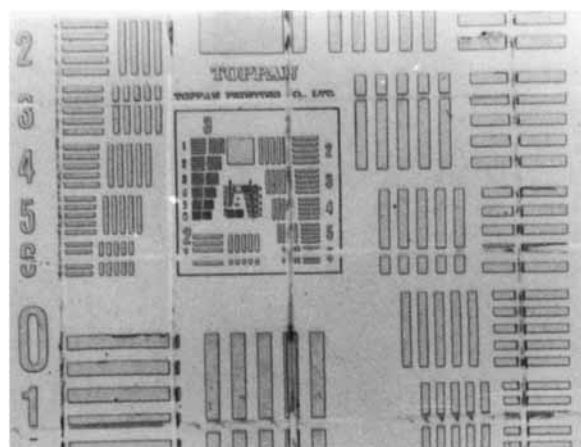


Figure 4 The exposure response curves of positive (α -PMTMMS with BP-t-DNS) and negative (PMTMSS with BP-t-DNS) resists.



(A) Positive Images



(B) Negative Images

Figure 5 Microphotographs of (A) the positive and (B) the negative image patterns after the adhesion test (ASTM-D3359-83: A 3M tape was used, and patterns on the silicon wafer were cut to 100 lattices within 1 cm²) ($\times 50$).

containing resists coated on the silicon wafer without the use of an adhesion promoter were evaluated by the adhesion test. Figure 5 shows that neither positive (A) nor negative (B) image patterns were stripped after the adhesion test. This advantage is attributed to the silicon proton on the phenyl group to make a fine adhesion to the silicon wafer. Figure 6 shows that the developed positive images (line patterns) by α -PMTMMS with BP-t-DNS are highly resistant to thermal deformation at 220°C

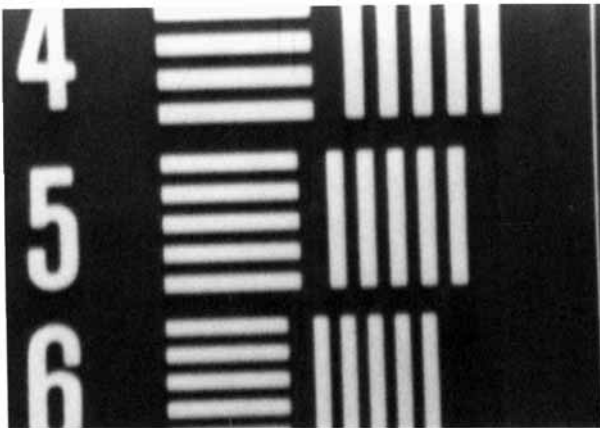
for 30 min. On the other hand, the developed negative images by PMTMSS with BP-t-DNS possess excellent thermal stability, yet images without deformation even at 300°C for 30 min, as shown in Figure 7. This advantage is due to the cross-linking reaction that occurred in the PMTMSS main chain.

Oxygen-Plasma Etching Resistance

A silicon-containing polymer for use as the top imaging layer in a bilayer resist system has attracted considerable interest because of its excellent durability to oxygen-plasma etching. It has been

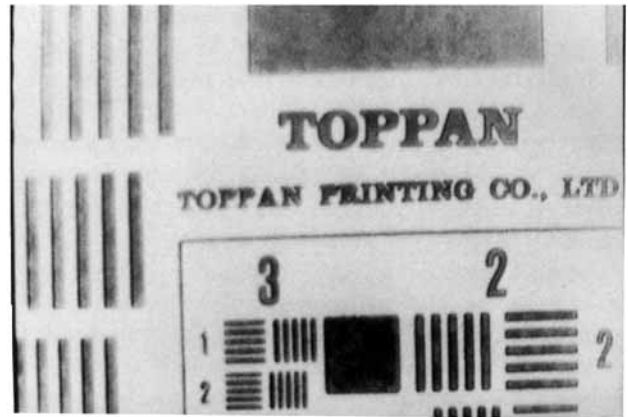


(A) No Bake



(B) 220°C/30 min.

Figure 6 Microphotographs of positive images based on α -PMTMMS resist after postbaking ($\times 100$).



(A) 250°C/30 min.



(B) 300°C/30 min.

Figure 7 Microphotographs of negative images based on PMTMSS resist after postbaking ($\times 100$).

reported⁸ that about 10 wt % silicon content can drastically lower the oxygen-plasma etching rate of organic polymers. ESCA analysis revealed that an oxygen-plasma converts silicon into silicon oxide or silicon dioxide. Consequently, the formation of a protective layer will inhibit oxygen-plasma from etching and doubles as an etching mask for the patterns transferring to the bottom layer (novolac resin or polyimide). The oxygen-plasma etching behavior of several polymer films was determined and compared to a hard-baked HPR-204, as shown in Table IV. The effects of some factors as polymer structure

Table IV The Oxygen-Plasma Etching Rate of Several Polymer Films^a

Code	Silicon Content (wt %)	\overline{M}_w	Etching Rate (Å/min)	Etching Selectivity ^b
α -PHTMMS	7.4	48,000	70	1 : 6
PHTMSS	7.7	126,000	60	1 : 7
α -PMTMMS	9.8	37,800	40	1 : 10.5
PMTMSS	10.3	31,000	35	1 : 12
PMS	—	29,600	350	—
Polyimide ^c	—	—	240	—
HPR-204	—	—	420	—

^a The oxygen-plasma condition had an RF level power of 1300 W and chamber pressure of 0.4 Torr.

^b Versus hard-baked HPR-204.

^c The polyimide was prepared from pyromellitic dianhydride and 4,4'-oxydianiline; η_{inh} : 1.2.

and molecular weight do not influence the etching rate much. Note the increase in etching selectivity from 6 to 12 for α -PHTMMS containing 7.4 wt % silicon and PMTMSS containing 10.3 wt % silicon, respectively. Selectivity of 1 : 12 is enough for PMTMSS to double as an etching mask. The most effective factor for increasing selectivity is to increase the silicon content. A polymer with higher silicon content survives longer in oxygen-plasma.

CONCLUSION

Several maleimide/styrenic monomer copolymers were synthesized. Sufficient alkaline solubilities were obtained at 50% maleimide units. The chain-stiffening effects of the maleimide and α -methylstyrene group were responsible for the high-temperature properties. The silicon-containing resists made a good adhesion to silicon wafer without an adhesion promoter. Microlithographic positive/negative images were obtained that were stable to temperatures higher than 200°C. PMTMSS contains 10.3 wt % silicon to show an oxygen-plasma etching rate of 1 : 12 compared to hard-baked HPR-204.

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REFERENCES

- S. R. Turner, R. A. Arcus, C. G. Houle, and W. R. Schleigh, *Polym. Eng. Sci.*, **26**, 1096 (1986).
- M. Iwasaki, H. Misu, and S. Miyano, U.S. Pat. 4,139,384 (Feb. 13, 1979) (to Fuji Photo Film Co.).
- G. J. Cernigliaro and C. R. Shipley, U.S. Pat. 4,439,516 (March 27, 1984) (to Shipley Company Inc.).
- H. Ito, C. G. Willson, J. M. J. Frecht, M. J. Farrall, and E. Eichler, *Macromolecules*, **16**, 510 (1983).
- H. Ito, C. G. Willson, and J. M. J. Frechet, in *Advances in Resist Technology and Processing IV*, SPIE, **771**, 24 (1987).
- C. E. Osuch, K. Brahim, F. R. Hopf, M. J. McFarland, A. Mooring, and C. J. Wu, in *Advances in Resist Technology and Processing III*, SPIE, **631**, 68 (1986).
- R. Sezi, M. Sebal, and R. Leuschner, *Polym. Eng. Sci.*, **29**, 891 (1989).
- G. N. Taylor, T. M. Wolf, and L. E. Stillwagon, *Solid State Technol.*, **27**, 145 (1984).
- B. J. Lin, in *Introduction to Microlithography*, L. F. Thompson, C. G. Willson, and M. J. Bowden, Eds., ACS Symp. Ser. 219, American Chemical Society, Washington, DC, 1983, Chap. 6.
- W. Y. Chiang and J. Y. Lu, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 399 (1991); *Chem. Abstr.*, **114**, 196210h (1991).
- W. Y. Chiang and J. Y. Lu, *Angew. Makromol. Chem.*, **205**, 75 (1993).
- J. M. Barrales-Rienda and J. G. Ramos, *J. Macromol. Sci. Chem.*, **A11**, 267 (1967).
- C. H. Stiteler, U.S. Pat. 3,265,708 (Aug. 9, 1966) (to U.S. Rubber Co.).
- Y. Ohnishi, M. Suzuki, K. Saigo, Y. Saotome, and H. Gokan, in *Advances in Resist Technology and Processing II*, SPIE, **539**, 62 (1985).
- L. F. Thompson, C. G. Willson, and M. J. Bowden, Eds., in *Materials for Microlithography*, ACS Symp. Ser. 266, American Chemical Society, Washington, DC, 1984, Chap. 3.

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