

Table X. Comparisons of the Observed and Calculated Powder Patterns of Ba₂SbI

<i>h k l</i>	<i>d</i> _{calcd} ^a	<i>d</i> _{obsd}	<i>I</i> _{calcd} ^a	<i>I</i> _{obsd}
2 0 0	3.549	3.547 (4)	100	100
2 2 0	2.509	2.508 (4)	79	70
2 2 2	2.049	2.042 (3)	30	20 ^b
4 0 0	1.774	1.774 (3)	15	20
4 2 0	1.587	1.586 (3)	44	50
4 2 2	1.449	1.449 (3)	34	20
4 4 0	1.255	1.253 (2)	12	

^aNaCl type. Reflections with *I*_{calcd} < 5.0 are not listed. ^bThe reflection is superimposed by one from Ba₄Sb_{2.5}I_{0.5}.

hexagonal setting, but without success. Consideration of the Ca₄Sb_{2.4}S_{0.4} structural result and of this data set in the alternative cubic setting led to the identification and solution of the structure as Ba₄Sb_{2.5}I_{0.5}, again an anti-Th₃P₄ type but this time with lattice sites fully occupied. Refinement data are reported in Tables I and IX. The Ba-Sb/I distances are comparable to the shortest Ba-Sb values found in Ba₅Sb₃Cl (Table IV). Any ordering of the antimony and iodine atoms would not be expected to be discernible because of their similar scattering abilities. The literature notes that Ba₄P_{2.5}I_{0.5} also adopts this structure.³⁸ An attempt to synthesize the analogous Ba₄Bi_{2.5}I_{0.5} did not succeed.

The evident stoichiometry of the second product in the reaction above is Ba₂SbI, but the powder data were not those for the anti-α-NaFeO₂ type identified for Ba₂PI.³⁸ However, the relatively simple pattern could be fit to a NaCl-type lattice with *a* = 7.0970 (6) Å, and the pattern calculated on this basis have a good description of the observed one (Table X). A NaCl structure is found for a number of alkaline-earth-metal compounds of this charge type when the disordered anions are of similar size; for example, Ca₂AsBr, (which is single phase to Ca_{2.5}AsBr₂), Sr₂AsCl,³⁹ and (Ca,Sr)PbCl,⁴⁰ but this is the first iodide to

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be so classified. The corresponding calcium iodides⁴¹ and Ba₂P(Cl,Br,I)³⁸ have been reported only in the alternative α-NaFeO₂ structure.

Overview. The A₅Pn₃ compounds formed between the alkaline-earth metals and the pnictides As, Sb, or Bi appear to be stoichiometric, and they occur in either an Mn₅Si₃ (M) or a β-Yb₅Sb₃ (Y) structure. These all have one excess valence electron and are probably, but not assuredly, metallic. Each structure type contains suitable interstitial sites so that isostructural A₅Pn₃X phases, Pn = Sb, Bi, can be obtained with X = Cl, Br in the former as well as Ca₅Pn₃F phases in the latter structure type. The larger sized iodide or the smaller amount of sulfide necessary for a valence phase are accommodated in the alternative Zintl phases Ba₄Sb_{2.5}I_{0.5} and Ca₄Sb_{2.4}S_{0.4} for the two A₅Pn₃ systems studied. Both have an anti-Th₃P₄ type structure. Oxide produces the already known Zintl phase Ca₄Sb₂O (K₂NiF₄ type),¹³ while carbon appears to be most stable as CaC₂.

Phases with the M structure that have greater numbers of excess valence electrons such as Zr₅Sb₃ and Zr₅Sn₃ also form comparable interstitial structures but without as great a restriction on the valence characteristics of the interstitial.^{10,11} Explorations with halogen in rare-earth-metal analogues show that M-type Ce₅(Sb,Bi)₃(Cl,Br) phases readily form as well. A field rich in new materials appears possible here. Quantification of other physical properties and the exploration of other systems are underway.

Acknowledgment. Larry Wolfe provided equilibration data for several of the binary systems in clarification of the phase relationships. We are indebted to R. A. Jacobson for the provision of diffraction and computing facilities.

Supplementary Material Available: Tables of anisotropic thermal parameters for Sr₅Sb₃, Ca₅Sb₃Cl, Ba₅Sb₃Cl, Ca₅Sb₃F, Ca₅Bi₃F (2 pages); listings of observed and calculated structure factors for the same phases and Ba₄Sb_{2.5}I_{0.5} (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Oxygen Reactive Ion Etching of Novolac-Siloxane Block Copolymers

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The coupling reaction between dimethylamine-terminated poly(dimethylsiloxane) (PDMSX) oligomers and the phenolic hydroxyl groups of novolac resins results in block copolymer systems. The charge ratio of PDMSX oligomers will control the silicon content of the final material, which determines the solubility and O₂ reactive ion etching (RIE) resistance. Three different copolymers were prepared by using *o*-cresol and 2-methylresorcinol novolacs and poly(hydroxystyrene) as the phenolic component. At ~12 wt % silicon content these copolymers exhibited a good O₂ RIE selectivity with respect to hard-baked HPR-206 of ~1:12, which is adequate for a dry pattern transfer process. These copolymers have potential use as positive bilayer resists because of their solubility in aqueous base developers.

Introduction

Positive photoresists based on novolac resin/diazonaphthoquinone sensitizer systems have been extensively utilized due to their desirable combination of availability

and materials properties,¹ such as lithographic sensitivity and aqueous base solubility. Unfortunately, their lack of

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(1) Willson, C. G. In *Introduction Microlithography*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; ACS Symposium Series No. 219; American Chemical Society: Washington, DC, 1983; p 87.

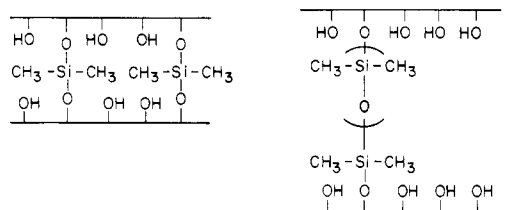


Figure 1. Schematic representation of siloxane oligomer molecular weight.

adequate oxygen etching resistance has precluded their use in bilevel resist applications. In recent years, researchers have improved the O_2 plasma etching properties of these materials by attempting to incorporate organosilicon moieties into polymers that can function as resists.^{2-10,17} However, it is a difficult problem to design a resist with an adequate amount of silicon to improve RIE resistance while maintaining aqueous base solubility and a sufficiently high glass transition temperature (T_g) for better dimensional control of submicron features.

Smith² found that the incorporation of silicon into novolac resins via extensive phenolic hydroxyl functionalization resulted in low T_g polymers (20–30 °C) that were tacky and, more importantly, lacked adequate aqueous base solubility to be useful as positive resist materials. Other studies have employed silyl-containing monomer units^{8,18} which also resulted in materials with low T_g 's. If such a material were used in a contact exposure, poor pattern resolution may be experienced due to resist adhesion to the mask. Additionally, if sample heating occurs during the O_2 RIE pattern transfer process to temperatures above the polymer's T_g , line broadening due to resist flow may result.

From a polymer "architecture" perspective, the loss in aqueous base solubility does not stem solely from the hydrophobicity of the organosilicon substituent but also results from the loss of phenolic hydroxyl functionalities (Figure 1). A lowering of the T_g results from the incorporation of a bulky side group, such as a trimethylsilyl group, which effectively increases the polymer's free volume. If a silicon-containing precursor were oligomeric in nature, its copolymerization with a preformed phenolic resin could be controlled to optimize the silicon content of the material while minimizing the loss of phenolic functional groups (Figure 1). This preparation of block copolymers would alleviate the free-volume effect of a large silicon side group while providing a sufficiently high silicon content. Maintaining a larger volume percent phenolic resin than silicon oligomer should result in a copolymer that exhibits novolac properties. The copolymerization of functionally terminated oligomeric siloxanes with no-

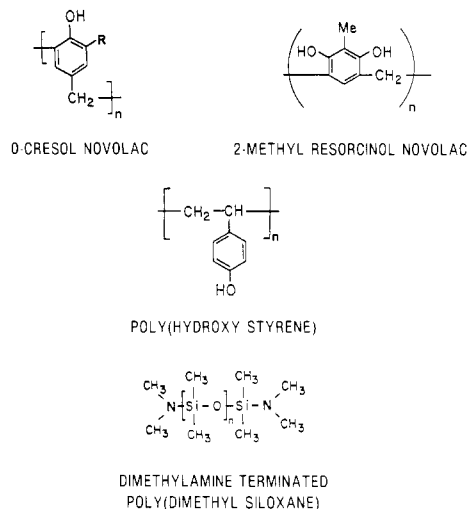


Figure 2. Structures of oligomers and copolymers.

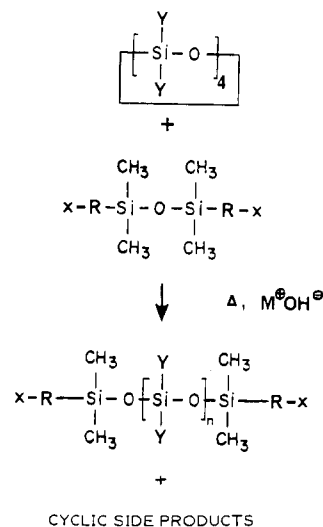


Figure 3. Synthesis of poly(dimethylsiloxane) oligomers.

volac resins appears as a viable route to the preparation of positive bilevel resists.

The chemical structure (Figure 2) and molecular weight of both the siloxane and the novolac are the two most critical variables. An investigation of the structure-property relationships between a series of siloxane–novolac copolymers was undertaken focusing initially on their O_2 RIE resistance and aqueous base solubility. An *o*-cresol-based novolac copolymer series was used to determine the effect of increasing silicon content on O_2 RIE behavior. A 2-methylresorcinol resin was used in an attempt to increase the aqueous base solubility of the siloxane copolymers. A novolac resin substitute, poly(hydroxystyrene), was also studied due to its lower absorbance in the deep UV as compared to standard novolac resins.

Experimental Section

o-Cresol (Aldrich) was purified by two successive vacuum distillations, taking the middle boiling, 80%, fraction each time. 2-Methylresorcinol (Aldrich) was recrystallized twice from hot toluene, and decolorizing charcoal was used. Tetrahydrofuran (THF) was distilled from a characteristic purple-colored sodium benzophenone slurry. All other materials were used as received from various sources.

Oligomer Synthesis. Dimethylamine-terminated poly(dimethylsiloxane) oligomers (PDMSX) were prepared by the anionic ring-opening polymerization of octamethylcyclotetrasiloxane, D_4 , with a tetramethylammonium siloxanolate catalyst¹¹ in the

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(5) Taylor, G. N.; Wolf, T. M. *Polym. Eng. Sci.* 1980, 20, 1087.

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(9) Shaw, J.; Babich, E.; Hatzakis, M.; Paraszczak, J. *Solid State Technol.* 1987, 30, 61.

(10) Noguchi, T.; Nito, K.; Seto, J.; Hata, I.; Sato, H.; Tsumori, T.; *Proc. SPIE Adv. Resist Technol. V* 1988, 920, 168.

presence of a low molecular weight dimethylamine-terminated PDMSX (Petrarch) as an end-blocking reagent (Figure 3). These reactions were run in bulk under an inert atmosphere for 48 h at 80 °C. The tetramethyl siloxanolate catalyst was decomposed when heated at 120 °C for 24 h. High-temperature vacuum stripping was employed to remove cyclic oligomeric byproducts. These air- and moisture-sensitive oligomers were stored in a sealed serum vial in a desiccator.

o-Cresol-based novolacs were prepared by two methods. In the first approach, the purified *o*-cresol and oxalic acid dihydrate were charged into the reaction flask and dissolved to 20 wt % with water. An equimolar quantity of a 37% aqueous formaldehyde solution was added dropwise over a period of 3 h via an addition funnel. A N₂ atmosphere and reflux conditions (94 °C) were maintained during addition. After 6 h, a two-phase mixture was present, and toluene was added to form an azeotrope with water, which was collected in a Dean-Stark trap. Upon dehydration of the system, the catalyst precipitated from solution. Consequently, 2-ethoxyethyl acetate was added to redissolve the catalyst, and the reaction continued for 4 h at 110 °C. The reaction mixture was then filtered, cooled, and precipitated into petroleum ether. The tan powder was redissolved in chloroform, filtered to remove oxalic acid dihydrate, and reprecipitated in petroleum ether. A fine powder was obtained which was redissolved in acetone, precipitated in water, and dried under vacuum at 20 °C in 85% yield.

The second method employed *p*-toluenesulfonic acid (*p*-TSA) as the catalyst, and the reaction was run in toluene. The formaldehyde solution was added dropwise over 1 h. After 6 h at 100–115 °C, the solution was again dehydrated via toluene/water azeotrope, and the reaction mixture became viscous. Following the same workup as previously described, a light pink powder was obtained in a 92% yield.

2-Methylresorcinol-based oligomers were prepared in toluene by using *p*-TSA as the catalyst. The reaction was run at 80 °C, and as the formaldehyde solution was added, the colorless solution quickly became yellow and then orange. After 2 h, the reaction was stopped and worked up as usual, yielding a reddish-brown polymer in 84% yield.

Copolymer Synthesis. All novolac resins were dried under vacuum at 30 °C until a constant weight was achieved. The dried novolac resins were dissolved in freshly distilled tetrahydrofuran (THF) to 15 wt % solids under a nitrogen atmosphere. Dimethylamine-terminated PDMSX oligomers were dissolved to 15 wt % with THF in an addition funnel. The siloxane solution was slowly added to the refluxing novolac solution under nitrogen atmosphere. The reaction was run for 1 h after complete addition of the siloxane solution by using a rapid nitrogen flow to remove the gaseous byproduct. The reaction mixture was then precipitated into water and dried in a vacuum oven at 30 °C. Yields were typically >98%.

Poly(hydroxystyrene-dimethylsiloxane) copolymers were prepared by using poly(hydroxystyrene) obtained from Hoechst Celanese, $M_w = 30\,000$ g/mol. It was dissolved in dry THF to 10 wt % solids, and the siloxane oligomer was added as a 40 wt % solution in THF. Upon complete addition (2 h), the reaction was refluxed for 4 h. The reaction mixture was precipitated into water, and the white fibrous polymer was dried under vacuum at 60 °C, yield 97%.

The experimental determination for the percent silicon in a copolymer was made by calculating the percent siloxane incorporated into the copolymer (M_n of oligomer minus the molecular weight of the end groups, divided by M_n) and multiplying by the initial weight of the siloxane oligomer charged. This gave the total incorporated weight of the siloxane oligomer. The weight of the siloxane divided by the total weight of the system gave the experimental percent siloxane in the copolymer. Multiplication by the percent silicon contained in a dimethylsiloxane repeat unit yielded the weight percent silicon.

Deep UV exposures were performed by using a Karl Suss MA 56M contact aligner fitted with a Lambda Physik KrF laser (248 nm) with an output of 13 mJ cm⁻² s⁻¹ at 100 Hz.

Table I. Molecular Weight Determination of Poly(dimethylsiloxane) Oligomers

sample	\bar{M}_n		
	theory	NMR	titration
1	5000	4370	4260
2	2000	1780	1710
3	700	630	610

Table II. Molecular Weight Determination of a Series of *o*-Cresol Novolac Oligomers

sample	catalyst	$[\eta]^a$	VPO ^b
A	oxalic acid	2230	2080
B	oxalic acid	1980	2150
C	oxalic acid	8890	
D	oxalic acid	6180	
E	<i>p</i> -TSA ^c	2270	2410
F	<i>p</i> -TSA ^c	2510	

^aIntrinsic viscosities run at 30 °C in methyl ethyl ketone. ^bVapor phase osmometry run in methyl ethyl ketone. ^c*p*-Toluenesulfonic acid hydrate.

Characterization. The molecular weight, \bar{M}_n , of the dimethylamine PDMSX oligomers were determined by both proton NMR and nonaqueous potentiometric titration (Table I). In the proton NMR, a ratio of the dimethylamine protons to the silicon methyl protons yielded the number of monomer repeat units contained in the oligomer. Multiplication by the molecular weight of the monomer unit [$-\text{O}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2-$] yields the \bar{M}_n for the oligomer. Titrations utilized 1 g of PDMSX oligomer in 100 mL of isopropyl alcohol with bromothymol blue as a visual indicator.¹¹ The titrant was 0.1 N HCl in isopropyl alcohol (Fisher Scientific). The theoretical molecular weight values calculated for each siloxane oligomer determined the initial charge ratio of the cyclic siloxane tetramer to low molecular weight amine terminated oligomer. Both proton NMR and titrated \bar{M}_n values agreed with the desired values.

Vapor phase osmometry (Corona Wescam) and intrinsic viscosity (η) measurements were used to determine molecular weights of the novolac resins (Table II). ¹H NMR spectroscopy was used to confirm molecular structure of the starting oligomers and final copolymers. The silicon content of the different materials was determined by elemental analysis (Galbraith Laboratories).

The *o*-cresol-based novolac-siloxane copolymers were dissolved to 20 wt % in 2-methoxyethyl acetate. Ten wt % solutions in 2-methyltetrahydrofuran were prepared for the poly(hydroxystyrene-dimethylsiloxane) and (2-methylresorcinol-dimethylsiloxane) copolymers. All solutions were filtered through successive 1.0-, 0.5-, and 0.2- μm filters (Fluoropore, Millipore Corp.). Hexamethyldisilazane (HMDS) vapor primed 4-in. silicon wafers were coated with nominal 0.5- μm -thick resist films and were divided into eight sections for etching studies. The etching experiments were run using a Plasma Technology parallel plate etching unit at -350-V bias, 90-W power, and 20 sccm O₂ at a pressure of 30 mTorr. Aluminum electrodes were used. For the same etching times, each copolymer sample was run simultaneously with a hard-baked HPR-206 wafer as reference. Thickness measurements before and after O₂ plasma etching were performed with a Dektak IIA profilometer.

Results and Discussion

A series of siloxane-containing block copolymers have been prepared to assess the viability of poly(dimethylsiloxane), PDMSX, as a component of a positive bilevel resist formulation. Our synthetic methodology employed the reaction of preformed oligomeric species in a copolymerization scheme to yield block copolymer systems. A single high molecular weight PDMSX oligomer was used as one precursor while the nature of the phenolic oligomer varied. Initially, an *o*-cresol-based novolac resin was used due to its good aqueous base solubility and its reproducible synthesis. A 2-methylresorcinol-based novolac oligomer was also studied, as it contained an additional phenolic

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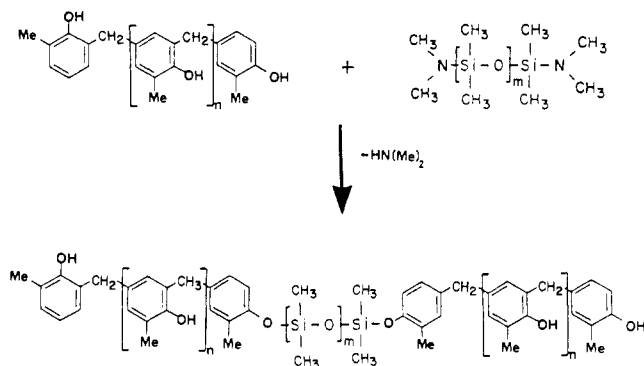


Figure 4. Synthesis of *o*-cresol novolac-siloxane copolymer.

Table III. Characteristics of *o*-Cresol Novolac-Siloxane Copolymers

\bar{M}_n siloxane block	% Si	TMAH solubility	etching ratio vs HPR after 15 min
4400	16	yes	13.5
4400	12	yes	13.4
4400	5	yes	5.3
4440	3	yes	3.2
1800	3	yes	3.4

hydroxyl group per repeat unit and should be expected to increase the aqueous base solubility as well as the glass transition temperature in comparison to the *o*-cresol-based system. Finally, poly(*p*-hydroxystyrene) was investigated as a substitute for novolac resins.

In the copolymer systems prepared, approximately 3% of the phenolic groups have been reacted with the PDMSX oligomer. The molar quantity of phenolic hydroxyl groups was determined by dividing the \bar{M}_n of the polymer by the molecular weight of the repeat unit. The number of moles of silylamine groups were found in an analogous manner. The copolymer yields in all cases were >97%. Water was vigorously excluded during synthesis to minimize hydrolysis of the silylamine functionality. The rapid and quantitative nature of the silylamine-phenol reaction has been well documented,^{12,16} and therefore, no free dimethylsiloxane should be present in the systems prepared here. All phenolic groups should possess equal reactivity toward the functionalized PDMSX oligomer, and for the sake of clarity, Figure 4 illustrates the A-B-A triblock structure resulting from two novolac resin chains (A) which have reacted at their termini with one PDMSX oligomer (B). The difunctional PDMSX may also react with the same novolac molecule at two different sites along the chain. This will result in an A-B diblock molecule that will be cyclic in nature. The size of this structure would be expected to vary according to the distance between the two phenolic groups on the novolac resin with which it

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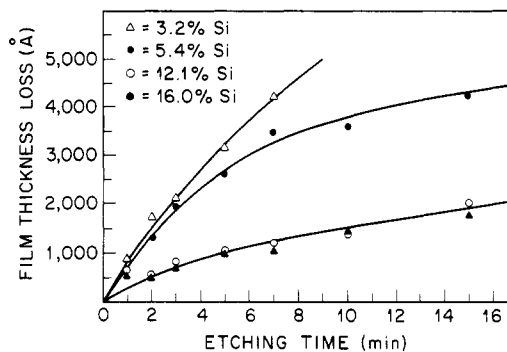


Figure 5. Film thickness loss during O_2 plasma etching vs etching time for *o*-cresol novolac-siloxane copolymers.

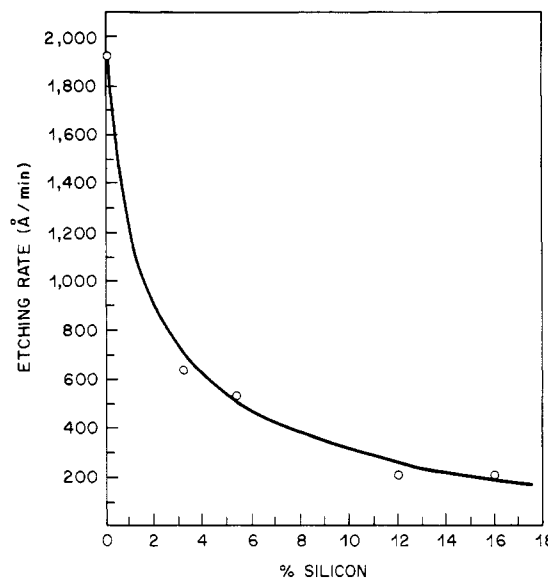


Figure 6. Oxygen etching rate vs percent silicon for *o*-cresol novolac-siloxane copolymers.

reacted. Due to the low number of phenolic groups reacted, some unreacted novolac resin will be present. Therefore, each copolymer system prepared will consist of a blend of block copolymer and novolac resin.

The hydrolytic stability of the Si-O-C bond has been addressed in polymeric systems, and it is much greater than that observed in small molecules.^{12,16} Several reasons for this unexpected stability were noted: among them; the hydrophobicity of the PDMSX block, microphase separation, the inaccessibility of the Si-O-C linkage, and the low number of these linkages overall.

The *o*-cresol novolac-dimethylsiloxane copolymer series (Table III) utilized a single batch of the novolac resin "A" (see Table II) and various weight percents of a constant molecular weight dimethylamine-terminated PDMSX. The block copolymers produced had silicon contents ranging from 3 to 16 wt %. Since the block length of each oligomer was the same within this series of copolymers (Table III), the only variable was the weight percent PDMSX incorporated.

The O_2 RIE resistance of the *o*-cresol novolac-dimethylsiloxane copolymer series containing 3.2, 5.4, 12.1, and 16.0 wt % silicon was tested by using HPR-206 as a reference. A plot of film thickness loss versus etching time is shown in Figure 5. The two copolymers with low silicon content exhibit a large initial film thickness loss as compared to the two high silicon content materials. There appears to be no improvement in the O_2 RIE resistance by incorporating a larger amount PDMSX, from 12 to 16 wt %, as demonstrated by the negligible difference in their

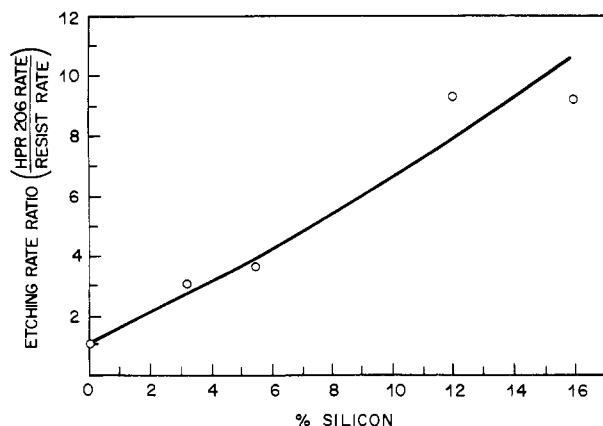


Figure 7. Oxygen etching selectivity vs percent silicon in *o*-cresol novolac-siloxane copolymers.

etching characteristics (Figure 5). In all samples with silicon contents greater than 5 wt % the etching rate becomes relatively constant after 7–8 min of etching, due to the formation of an inorganic silicon barrier layer which causes a decrease in the etching rate.⁵ The etching rate as a function of silicon content was determined after 10 min RIE and is shown in Figure 6. The starting novolac homopolymer (0 wt % silicon) etched at the same rate as HPR-206, 1920 Å/min. The typical asymptotic relationship between O₂ etching rate and percent Si found in other systems,^{5,7,13} is noted here. A large initial decrease in the etching rate is found at small percent silicon incorporation which becomes constant at 12–16 wt % silicon. The etching selectivity, or the etching rate ratio of the *o*-cresol novolac-dimethylsiloxane copolymer with respect to hard-baked HPR-206 as a function of percent silicon, can be seen in Figure 7. After 15 min, an etching selectivity of 1:13 was obtained with both the 12 and 16 wt % silicon copolymers (Table III). A value of 1:10 is often quoted as a minimum value necessary for dry pattern transfer via plasma development.

Unsensitized films prepared from all four copolymer compositions exhibited solubility in dilute tetramethylammonium hydroxide (TMAH) solutions, indicating their potential for use as positive resists. These solubilities are a good indication that the "blocky" structure of the silicon-containing moiety does not adversely affect the solubility in the high silicon containing materials. In view of the good O₂ RIE characteristics and aqueous base solubilities, the 12 and 16 wt % Si containing materials may be useful as positive bilevel resist components.

The effect of novolac structure in block copolymers with PDMSX was tested by preparing a 2-methylresorcinol-based novolac resin. The repeat unit of this polymer contains two phenolic hydroxyl groups as compared to a single one in the *o*-cresol-materials (Figure 2). This should result in a greater degree of aqueous base solubility due to the greater degree of hydrogen bonding. Preliminary solubility studies confirmed this as a 1.7- μ m-thick film of this resist material with 11 wt % silicon was dissolved by a 4% TMAH solution in 30 s.

The results of O₂ RIE experiments on this copolymer are summarized in Table IV. An O₂ RIE rate of 70 Å/min and an etching selectivity vs hard-baked HPR-206 of 1:28 was obtained. This material etches at a rate of less than one-half that obtained with the *o*-cresol-based siloxane copolymers. This may be due in part to the greater polarity of the starting oligomer, a higher T_g (Table V), or the possibility of microphase separation. The calculated solubility parameter^{14,15} for the 2-methylresorcinol oligomer is 11.9 (cal/cm³)^{1/2} and that for the *o*-cresol-based novolac

Table IV. Oxygen RIE Results Versus Copolymer Structure

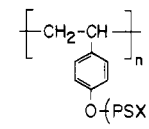
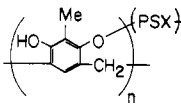
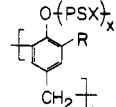
structure	% Si	O ₂ RIE rate, Å/min	etching rate ratio vs HPR
	12	160	1:12
	11	70	1:28
	12	140	1:14

Table V. Thermal Analysis of Novolac-Siloxane Copolymers

phenolic component	siloxane \bar{M}_n	wt % Si ^a	T_g , °C ^b
<i>o</i> -cresol novolac		0	76.3
	4400	16	78.9
	4400	12	77.2
	4400	5.4	77.1
2-methylresorcinol novolac	4400	3.2	74.3
		0	186.7
poly(hydroxystyrene)	4400	11	184.3
		0	171.8
	4400	12	174.3

^a From elemental analysis. ^b Differential scanning calorimetry values.

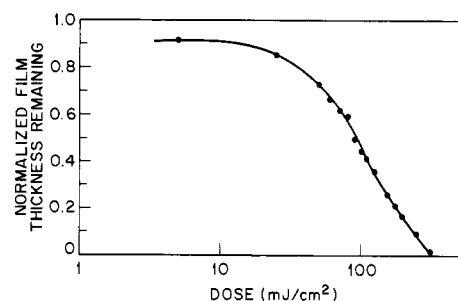


Figure 8. Exposure-response curve for 2-methylresorcinol-siloxane copolymer at 30 wt % sensitizer.

is 10.8 (cal/cm³)^{1/2}. Poly(dimethylsiloxane) has a solubility parameter of 7.3 (cal/cm³)^{1/2}. On the basis of these values, a greater degree of microphase separation may be expected with the 2-methylresorcinol copolymer. PDMSX is known to migrate to the air/polymer interface due to its low surface free energy, and the preferential coating of the resist surface with organosilicon material may result in the improved O₂ RIE etching of the 2-methylresorcinol copolymer over that of the *o*-cresol novolac copolymer.

Initial lithographic studies were performed on the 12 wt % silicon *o*-cresol novolac-siloxane system using 20 and 30 wt % (based on polymer weight) of a diazonaphthoquinone dissolution inhibitor (Fairmont Chemical Corp., positive sensitizer no. 1009). The optimum developer for the 20 wt % sensitized system was a 0.075% aqueous TMAH solution for 60 s. An exposure-response curve indicated low contrast ($\gamma = 0.6$) and extensive film thickness loss in the unexposed regions of the resist. Using a greater amount of dissolution inhibitor (30 wt %) resulted in improved contrast ($\gamma = 1.1$) and significantly less thinning in the unexposed regions (Figure 8). Excimer laser (248 nm) contact exposure of the 30 wt % sample at

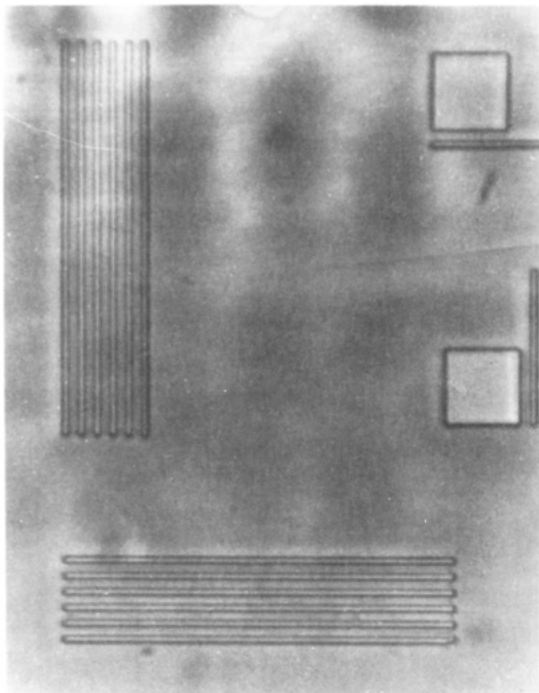


Figure 9. Optical microscope photograph of 0.5 μm line/space patterns for 2-methylresorcinol-siloxane copolymer at 160 \times magnification.

a dose of 195 mJ/cm^2 , followed by aqueous TMAH development resulted in the definition of 0.5 μm line/space patterns as viewed through an optical microscope (Figure 9). Under O_2 plasma etching, no difference in the observed O_2 etching rates between samples exposed to wet (TMAH) development and untreated samples was observed. This was a good indication that little Si-O-C bond cleavage and subsequent removal of free PDMSX occurred during wet development.

A third and final test of the synthetic utility of the silylamine-phenol reaction was found with poly(hydroxystyrene), PHS. PHS has much greater aqueous base solubility in TMAH and a lower absorbance at 248 and 254 nm than novolac resins. The copolymerization yielded an 11 wt % silicon material that exhibited O_2 RIE results similar to those obtained with the *o*-cresol-based starting oligomer (Table IV). An etching selectivity of 1:12 compared to hard-baked HPR-206 was obtained. Thin films cast from this copolymer also exhibited solubility in diluted TMAH solutions.

Figure 10 illustrates the O_2 RIE behavior for the three different siloxane copolymer systems prepared. Each copolymer possessed approximately equal silicon contents (Table IV), used the same molecular weight siloxane precursor, and were etched under identical conditions. Clearly, the 2-methylresorcinol-based copolymer had the best O_2 RIE resistance. The "blocky" polymer architecture is expected to be consistent throughout these samples, and, hence, the difference in the O_2 RIE resistance may also result from the structure of the phenolic component used.

Conclusions

The coupling reaction between dimethylamine-terminated poly(dimethylsiloxane) oligomers and various phe-

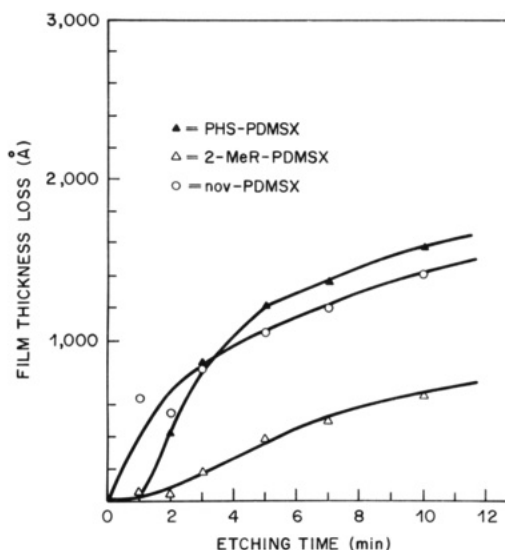


Figure 10. Film thickness loss vs etching time for three different siloxane copolymers with similar silicon contents.

nolic hydroxyl-containing oligomers results in block copolymer systems.¹⁶ In all the copolymers prepared, the percent silicon incorporation could be controlled by adjusting the charge ratio of the starting oligomers. Copolymers with *o*-cresol, 2-methylresorcinol, and poly(hydroxystyrene) yielded films soluble in aqueous base with silicon contents sufficient for dry pattern transfer processes. In the *o*-cresol-based novolac resin copolymer series, a material containing 12 wt % silicon exhibited optimal O_2 RIE resistance. Increasing the silicon content up to 16 wt % did not markedly improve the etching selectivity. The poly(hydroxystyrene-dimethylsiloxane) copolymer exhibited O_2 RIE behavior similar to the *o*-cresol novolac based system at a comparable weight percent Si.

The 2-methylresorcinol-based siloxane copolymer exhibited the best overall O_2 RIE resistance as well as excellent solubility in TMAH. Preliminary lithographic evaluations indicate the potential for submicrometer imaging and in combination with its O_2 RIE characteristics, the 2-methylresorcinol-dimethylsiloxane copolymer may be useful as a bilevel resist material.

Lithographic evaluations of all copolymers are in progress and shall be reported shortly. Further studies of morphology via transmission electron microscopy may elucidate the source of the difference in O_2 etching resistance between the 2-methylresorcinol-dimethylsiloxane copolymer and the remainder of the materials studied. Low-temperature differential scanning calorimetry will be performed to ascertain the extent of phase mixing between the PDMSX segments and the novolac resin matrices. Additionally, Auger depth profiling experiments will be run to determine additional morphological information.

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Registry No. (*o*-Cresol)(formaldehyde)(octamethylcyclotetrasiloxane) (block copolymer), 120060-02-8; (formaldehyde)-(2-methylresorcinol)(octamethylcyclotetrasiloxane) (block copolymer), 120060-03-9; (*p*-hydroxystyrene)(octamethylcyclotetrasiloxane) (block copolymer), 120060-04-0; O_2 , 7782-44-7.