Influence of Polymer Structure on the Miscibility of Photoacid Generators

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Analysis of a variety of polymer and photoacid generator (PAG) combinations was carried out using Rutherford backscattering spectrometry (RBS). The data are used to determine the concentration depth profiles for silicon, sulfur, and arsenic throughout the polymer films. The depth distribution of the arsenic and/or sulfur-containing PAG was of primary interest. We found that the compatibility or miscibility of the PAGs with the polymer matrices must be taken into consideration in order to create an effective photoresist. The distribution of various PAGs in different polymer matrices will be discussed, and the results correlated in terms of chemical structures.

Introduction

In previous work, we have synthesized and evaluated polymers of [(trimethylsilyl)oxy]styrene (TMSS), [(tert-butoxycarbonyl)oxy]styrene (TBS), and/or sulfone for use as photoresists.[1] These materials were evaluated as photoresists using several different photoacid generators (PAGs) including 2,6-dinitrobenzyl tosylate, triphenylsulfonium triflate, and triphenylsulfonium hexafluoroarsenate. The polymers had reasonable lithographic sensitivities when formulated with photoacid generators, except for the [(trimethylsilyl)oxy]styrene homopolymer 1 (Scheme 1). With this particular matrix polymer, a residue of 200 Å remained on the surface of the silicon substrate after aqueous development. As the optical density of this polymer is low (0.19 Abs/μm), and the generated acid is strong enough to cleave the silyl ether, the lithographic results indicated that either the PAG or the photogenerated acid was segregating or perhaps volatilizing from the polymer matrix. To investigate this phenomenon, Rutherford backscattering spectrometry (RBS) experiments were performed to examine the distribution of the PAG and/or the photogenerated acid throughout the polymer matrix.

Both RBS and Auger electron spectroscopy (AES) experiments were performed on a variety of polymer and PAG combinations. The data were used to determine the concentration depth profiles for specific atoms throughout the polymer films. We found that the compatibility or miscibility of the PAGs with the polymer matrices must be taken into consideration in order to create an effective photoresist.[1] The distribution of various PAGs in the polymers is discussed, and the results are correlated in terms of chemical structures.

Experimental Section

Materials. The syntheses of triphenylsulfonium hexafluoroarsenate (2), 2-fluoro-6-nitrobenzyl tosylate (3), and 2,6-dinitrobenzyl tosylate (4) were performed as described else-

Scheme 1

POLYMER	x	y
1	1	0
6	1	1
7	3	1
8	1	3
9	0	1
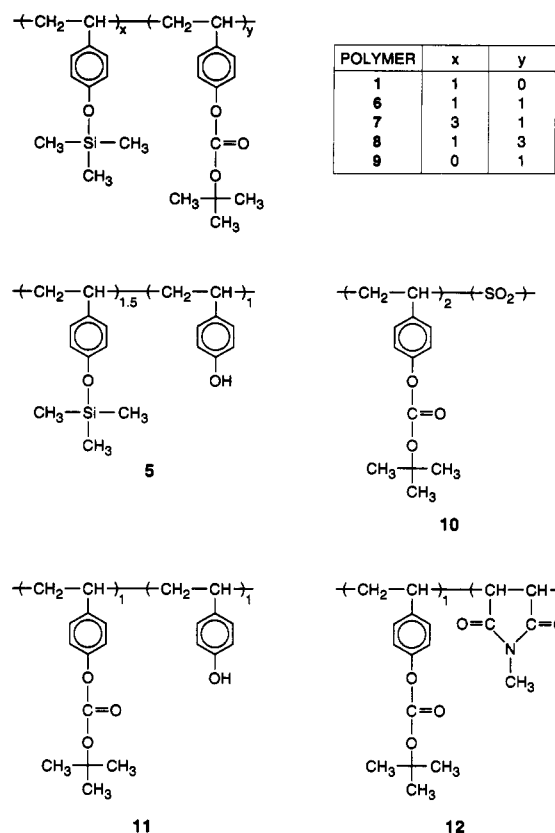
where.[2,3] The synthesis of the polymers containing silyloxystyrene is described in ref 1, while the syntheses of poly([(tert-butoxycarbonyl)oxy]styrene), poly([(tert-butoxycarbonyl)oxy]styrene sulfone), and poly(N-methylmaleimide-[(tert-butoxycarbonyl)oxy]styrene) may be found in refs 4–6, respectively.

Characterization. Thermal analysis data were obtained using a Perkin-Elmer TGA-7 thermogravimetric analyzer interfaced with a TAC 7 thermal analysis controller and a PE-7700 data station. DSC samples were heated at a rate of 20 °C/min.

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(6) Papadimitrakopolous, F.; Galvin, M., manuscript in preparation.

RBS spectra were recorded using a 2.120-MeV He^{+2} ion beam at a backscattering angle of 162°. The spectra were accumulated for a total ion dose of 40 μC using a 10-nA beam current. Thickness values were calculated using an assumed density of approximately 5.48 × 10^{22} atom/cm^3 (0.55 g/cm^3) for all samples. The values given in atomic percent were calculated assuming H/C atomic ratios of 0.9–1.4, depending on the particular material analyzed. By comparing heights of the various signals in the RBS spectra, we obtain atomic ratios (or molar ratios). For consistency, all elements present in the sample are ratioed, or normalized, with respect to carbon. The only element not measurable directly by RBS is hydrogen. Hence, the H/C ratio was calculated from the polymer formula. For the mix of polymers studied here, H/C varied from 1.1 to 1.5. The RBS data were then fit assuming a formula of $C_1H_{1.1-1.5}O_x(Si$ or $S)_y(As$ or $S)_z$ to determine values of x, y, z, etc., as needed for the particular polymer–PAG combination. Atomic percentages given in the tables were then simply obtained by dividing the number of atoms (or moles) of a particular element by the total number of atoms (or moles) multiplied by 100, e.g.

$$\text{atomic \% As} = \frac{100z}{1 + (1.1-1.5) + x + y + z}$$

The elements Si, S, and As are considered low-level impurities in a matrix consisting of C, H, and O.

In the plots of the RBS spectra, the x axis is given in channel number, which is related in a simple linear manner to the energy of the backscattered alpha particles. Backscattered signal at increasing channel no. (or energy) corresponds to higher mass elements, and the expected position for scattering from selected elements located at the surface of the polymer film is indicated by the arrows in the figure. The shape of a peak going toward lower channel number (with respect to the expected surface position) provides a measure of the concentration depth profile for that element. For the As, S, and Si signals, each channel corresponds to about 190 Å in thickness. This conversion from channel number to thickness requires knowledge of the film density, which for these samples was estimated to be ~5.5 × 10^{22} atom/cm^3.

AES depth profiles were obtained on a Perkin-Elmer Model 590 Auger electron spectrometer using a 5-keV primary electron beam.

Elemental analyses (C, H, Si) were determined by Robertson Microlit Laboratories, Inc. (Madison, NJ).

Synthesis of Poly(hydroxystyrene–[(trimethylsilyl)oxy]styrene), 5. Poly([(trimethylsilyl)oxy]styrene–[(*tert*-butoxycarbonyl)oxy]styrene) (4.01 g)[1] was pulverized and heated at 125 °C in a Kugelrohr oven for 24 h under vacuum. At 6-h intervals, the heating tube was cooled, a test sample taken, and the remaining material repulverized. The product was obtained as a white solid (1.99 g). ^{1}H NMR δ 0.27 (SiCH$_3$), 2.0–3.5 (CH and CH$_2$), 6.1–7.0 (ArH). IR (film): 914 cm^{-1}. Anal. Calcd: C, 72.1; H, 7.84; Si, 10.3. Found: C, 72.0; H, 7.70; Si, 10.5. $T_{decomposition}$: 399 °C. T_g: 140 °C.

Resist Formulation. Solutions were prepared by dissolving the PAG in a solution of the matrix polymer (15 wt/vol %) in ethyl ethoxypropionate (EEP). The amount of PAG was calculated relative to the weight of the polymer and was 5 wt % for the arsenate PAG (2) and 15 wt % for the tosylate PAGs (3, 4). These amounts were previously found to give optimum lithographic performance for TBS sulfone based chemically amplified resists.[2,3,5] The solutions were spin-coated onto 4-in. silicon substrates primed with HMDS and baked at 120 °C for 30 s. The resist-coated substrates were then exposed by a Süss Model MA56A contact aligner equipped with a Lambda Physik excimer laser operating at 248 nm at doses of approximately 170, 250, and 340 mJ/cm^2, respectively for resists utilizing PAGs 2, 4, and 3. After exposure, the substrates were baked at 120 °C for 4 min. Film thickness was measured on a Nanospec film-thickness gauge (Nanometrics, Inc.).

Results and Discussion

Photoacid Generator Miscibility with Poly([(trimethylsilyl)oxy]styrene). The distribution of the PAGs

Table 1. Compositional Characteristics of Selected Polymer/PAG Films

polym mater	PAG	UV exposure	thickness (Å)	Si	S	As
1	2	no	7600^a	3.3		0
			500^b	3.3		0.13
		yes	7600^a	3.3		0
			500^b	3.3		0.13
1	3	no	2000^a	3.1	0.16	
			6300^b	3.1	0.335	
		yes	6000	0.46	0.29	
6	2	no	6600^a	1.8		0.012
			1000^b	1.8		0.062
		yes	6300^a	1.5		0.010
			1000^b	1.5		0.078
6	4	no	8550	1.6	0.31	
		yes	6750	0.85	0.33	
7	2	no	6500^a	2.7		.003
			1500^b	2.7		.078
		yes	6700^a	2.65		.0037
			1200^b	2.65		.079
8	2	no	7600	0.91		.024
		yes	7600	0.79		.023
5	2	no	10800	2.06		.023
		yes	10500	1.85		.024
5	4	no	12500	1.26	.30	
		yes	13000	1.30	.29	

^{a} This value refers to the thickness of the "topmost" portion of the film. ^{b} This value refers to the thickness of the "bottommost" portion of the film.

in the silyloxy homopolymer 1 (Scheme 1) was initially investigated using RBS to follow the depth distribution of either As or S in the PAG. This technique gives quantitative results with a depth resolution of ~200 Å and is especially suited to analysis of heavy elements distributed in a light-element matrix. A comparison was made between samples that were baked after spin-coating and samples that were exposed to UV radiation, followed by a 4-min postexposure bake (PEB). The dose to effect complete dissolution of large area features was first determined on all the resist formulations and the exposure dose used for the RBS experiments was approximately twice the clearing dose.

The RBS results for composition and thickness are summarized in Tables 1 and 3. Composition information for the elements of interest is given in units of atomic percent. Please note in the tables that for those cases where elements are not distributed uniformly throughout the photoresist layer, the depth distribution is approximated using two layers of different composition—the first layer corresponding to the top and the second layer corresponding to the bottom (next to the Si substrate). Film thickness values were calculated from the RBS data using an assumed density of approximately 5.48 × 10^{22} atom/cm^3 (0.55 g/cm^3), although it is anticipated that the density of the films will change after exposure and PEB. The film thickness was also measured on a Nanospec film-thickness gauge and the values could be correlated to the values derived from the RBS experiments.

For the silyloxy homopolymer 1 formulated with the arsenate PAG 2 (Scheme 2), the distribution of arsenic in the resist films was monitored and the RBS thickness and composition results are summarized in Table 1. Significantly, the arsenic profile indicates that prior to exposure there is no arsenic in the top 7600 Å of the film (Figure 1) and that the arsenic species is strictly confined to a thin layer (~500 Å) at the polymer/substrate interface. This distribution is unchanged after exposure and PEB. The appearance of two distinct layers within the spin-cast
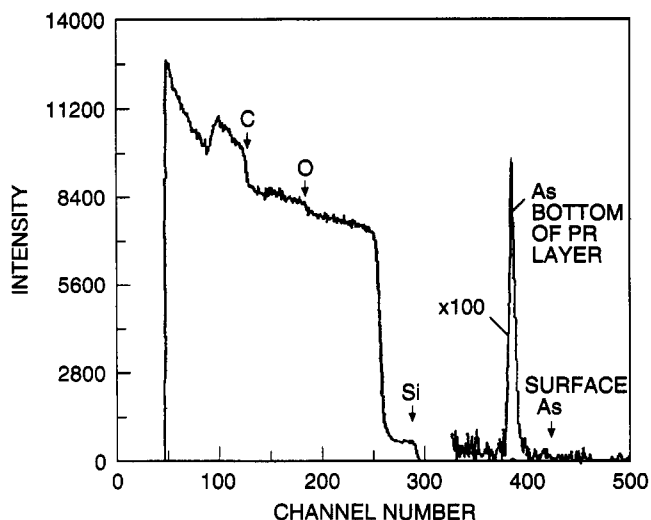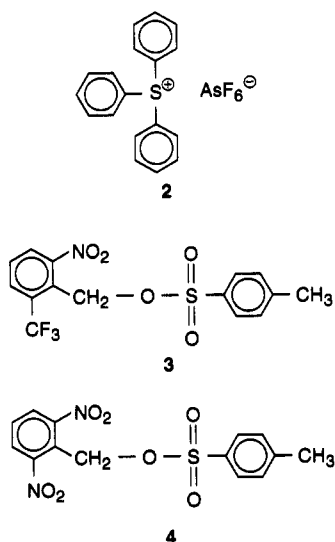
Figure 1. RBS spectrum for photoresist film containing polymer 1 and PAG 2.

Scheme 2

2

3

4

Figure 2. RBS spectrum for photoresist film containing polymer 1 and PAG 3 before exposure.

Figure 3. RBS spectrum for photoresist film containing polymer 1 and PAG 3 after exposure and PEB of the film.

Scheme 3

R = NO$_2$, CF$_3$

polymer film suggests that the arsenate PAG is by some mechanism migrating through the polymeric film to the substrate surface before exposure. Conceivably, the highly polar arsenate salt (2) has limited solubility or miscibility in the relatively hydrophobic polymer (1), leading to the observed layered phenomenon. Since a less polar PAG may be more miscible with the nonpolar (silyloxy)styrene material, alternative PAG chemistry was explored. Specifically, the non-ionic nitrobenzyl ester materials, 2-fluoro-6-nitrobenzyl tosylate (3) and 2,6-dinitrobenzyl tosylate (4, Scheme 2), were investigated. The dispersion of these PAGs throughout the silicon polymer (1) was compared to the distribution of the polar onium salt (2) in the same polymer matrix.

For the silyloxy homopolymer (1) formulated with the tosylate PAG 3, RBS analysis demonstrates that the sulfur arising from the PAG is distributed unevenly throughout the unexposed polymer film (Table 1, Figure 2). A sulfur content of ~0.16 atomic % is found in the top 2000 Å of the film, with an increase to ~0.33 atomic % in the bottom 6300 Å. After exposure and PEB, sulfur becomes more uniformly distributed throughout the polymer film (Figure 3), though only ~75% of the original number of sulfur atoms have remained in the matrix. Concurrently, there
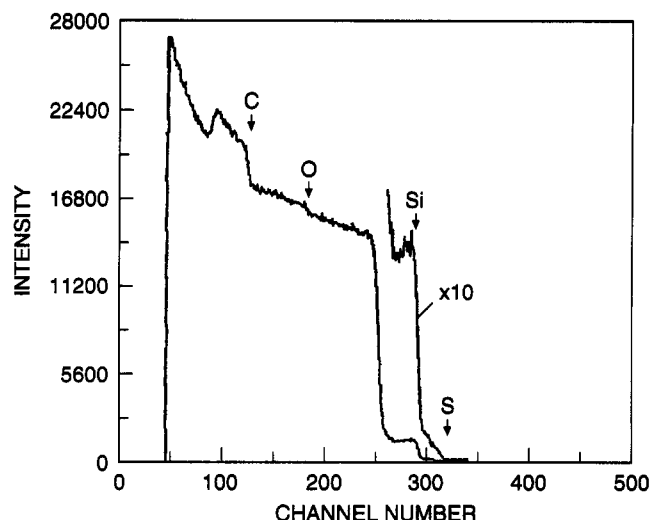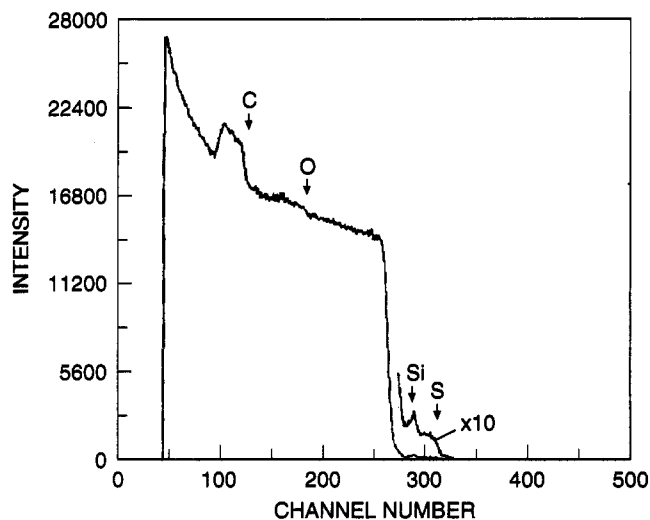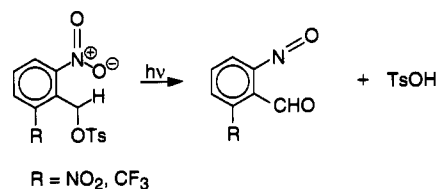
is a 28% reduction in film thickness and only 10% of the original number of silicon atoms remain.

This experiment provides much information about this polymer/PAG blend. First, the reduction in film thickness and loss of silicon upon exposure and PEB indicates that the photogenerated acid does cleave the silyl ether protecting group. Second, the silicon byproduct, hexamethyldisiloxane, volatilizes from the polymer film under the processing conditions employed here. Third, either the PAG or the photogenerated tosic acid additionally sublimes from the film leading to a decrease in the overall concentration of sulfur. An outline of the mechanism of acid generation from a tosylate PAG is shown in Scheme 3. The question of whether it is the PAG or the photogenerated acid that is migrating through the film
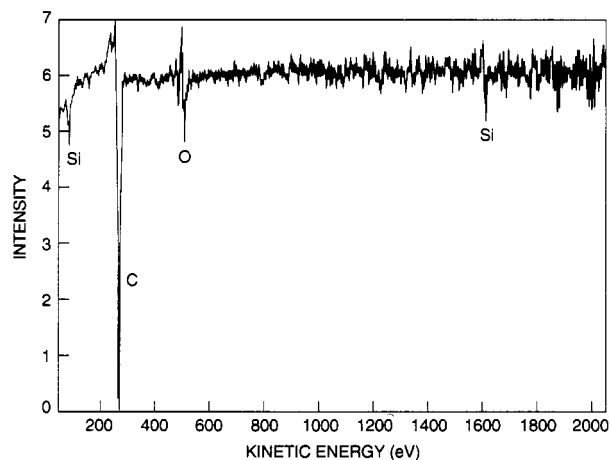
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Figure 4. Auger spectroscopy surface survey of polymer 1 and PAG 3 before exposure.

Figure 6. Auger spectroscopy surface survey of polymer 1 and PAG 3 after 4-min bake.

Figure 5. Auger spectroscopy surface survey of polymer 1 and PAG 3 after exposure and PEB.

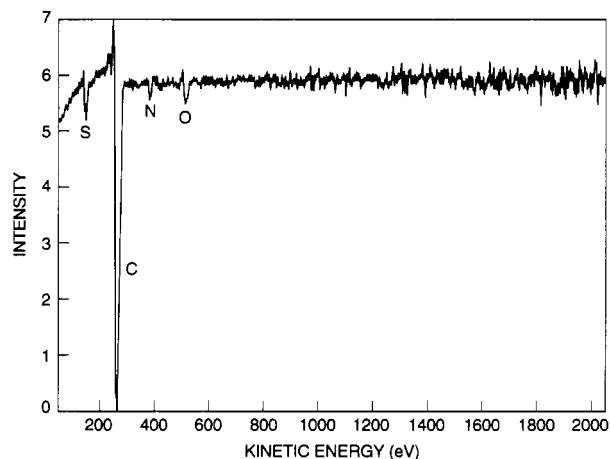**Figure 7.** Auger spectroscopy bulk scan of polymer 1 and PAG 3 before exposure.

was addressed with a simple experiment using Auger analysis.

Further information on the behavior of PAG 3 in polymer 1 was obtained by Auger electron spectroscopy (AES). The AES surface surveys probe ~15 Å of the polymer film surface and indicate which atoms are present on the surface of the film. A polymer film containing the silyloxy homopolymer (1) and tosylate PAG (3) was baked at 120 °C for 30 s to remove solvent. The AES surface survey clearly shows that the elements found in homopolymer 1, namely, silicon, carbon, and oxygen, are present (Figure 4). Sulfur, which emanates from the PAG, is noticeably absent. Upon exposure followed by a PEB at 120 °C for 4 min, carbon and oxygen, as well as sulfur and nitrogen originating from the PAG, are detected at the surface (Figure 5). After exposure then, either the PAG or the photogenerated acid has migrated to the polymer surface effecting cleavage of the silyl ether at the air/polymer interface. These results are consistent with the RBS data previously discussed. Auger spectroscopy was further used to determine whether it is the PAG or the photogenerated acid that migrates to the surface. Thus far, the data have shown that after exposure and PEB, sulfur moves from the bottom of the polymer film to the surface of the polymer/air interface. If sulfur migrates to the surface of an unexposed film that has been subjected to the 4-min 120 °C PEB condition, then it is clearly the PAG that migrates as the acid is generated only upon exposure to UV radiation. A sample of the silyloxy
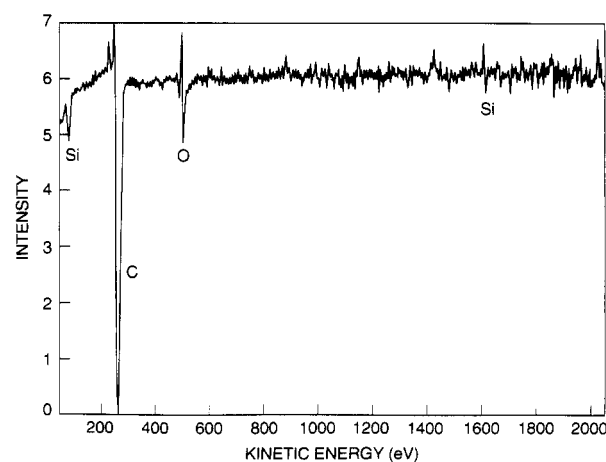
homopolymer 1 and tosylate PAG 3 was baked at 120 °C for 4 min. Only silicon, oxygen, and carbon from polymer 1 are observed at the polymer surface in an AES surface surveys scan (Figure 6).

A bulk survey scan was obtained from the same three samples that were used for Figures 4–6 after argon ion beam sputtering to determine which elements were present throughout the entire thickness of the polymer film. In the unexposed film, carbon, oxygen, silicon (from polymer 1), and sulfur (from the PAG, 3) are observed (Figure 7). After exposure and PEB, the concentration of silicon is significantly reduced, while carbon, oxygen, and sulfur are clearly still present (Figure 8). The spectra of the sample which was not exposed but baked for 4 min (Figure 9) look similar to the other unexposed sample (Figure 7). The results indicate that sulfur is still present in the polymer matrices.

The data presented above clearly demonstrate the importance of polymer/PAG design in effecting miscibility of even small molecules with polymer matrices. The combined RBS and Auger data presented above show that the PAGs used in this study are not miscible with the nonpolar, silylated homopolymer 1 affording films where the air/polymer interface is depleted in PAG. In the case of the nitrobenzyl ester PAG, AES results showed that upon generation of tosic acid, the acid itself was prone to migrate through and volatilize from the polymer film. The phenomenon of immiscibility between polymer materials and selected additives has been reported previously. In
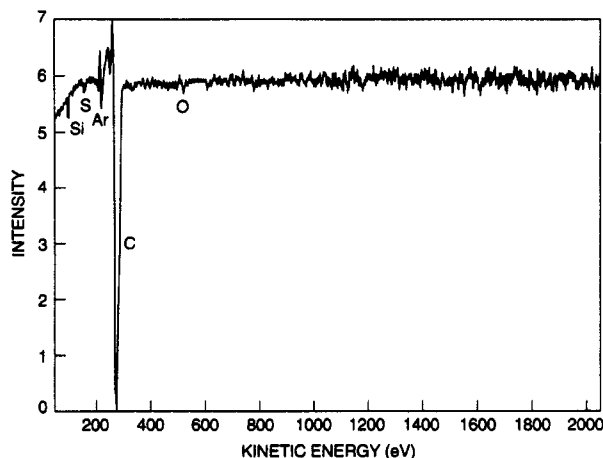
Figure 8. Auger spectroscopy bulk scan of polymer 1 and PAG 3 after exposure and PEB.
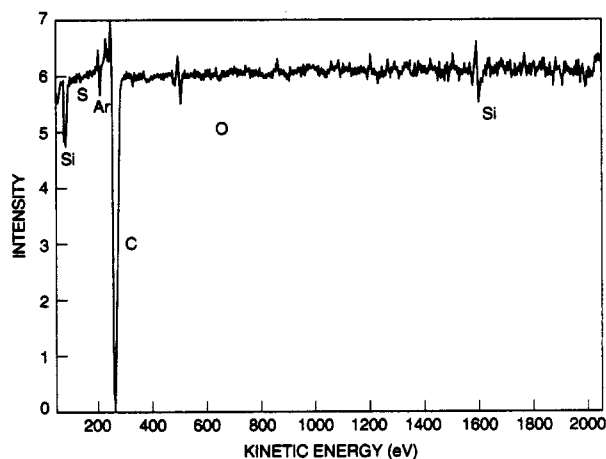

Figure 9. Auger spectroscopy bulk scan of polymer 1 and PAG 3 after 4-min bake.

Table 2. Thermal Characteristics of Selected Materials

sample	T_g (°C)	T_m (°C)
polymer 1	78	
PAG 2		199
polymer 1 + PAG 2	77	110
polymer 1 + PAG 4	76	

a related example, Hult et al. reported the appearance of phase separation between a styrenic polymer and an onium salt PAG.[7] Specifically, the migration of onium salts was followed by ESCA in polystyrene systems, and the air/polymer interface was found to be depleted in salt. More polar salts suffered greater surface depletion than the less polar materials. Similarly, Allen et al. investigated the morphology of substituted methacrylate/onium salt films and found a correlation between polymer structure and miscibility of the two components.[8]

Hult[7] additionally found that spin-coating of the resist solution further depletes the PAG concentration at the resist surface when the PAG has poor solubility in the polymer. Thus, the miscibility of the silyloxy homopolymer with the arsenate and tosylate PAGs was evaluated by preparing polymer films at "equilibrium". Resist solutions were diluted two times relative to the concentration of previous samples to ensure that the molecules were fully dispersed. The solutions were prepared by dissolving the PAG in a solution of the homopolymer 1 (7.5 wt/vol %) in tetrahydrofuran. The amount of PAG was calculated relative to the weight of the polymer and was 2.5 wt % for the arsenate PAG 2 and 7.5 wt % for the tosylate PAG 4. Equilibrium films were prepared by

casting the solution onto silicon substrates. The films were then dried under a constant flow of nitrogen at room temperature over 2 days. When dried, both samples were optically opaque. The sample containing the arsenate PAG 2 exhibited a cracked surface which could result from either stress due to the evaporation of the solvent or crystallization of the arsenate PAG. The glass transition temperature (T_g) of this polymer blend was 77 °C with an exothermic peak at 110 °C (Table 2). One could visually ascertain that the tosylate PAG 4 and silyloxy homopolymer 1 blend was also phase separated: the T_g of this sample was 76 °C. As the T_g of the pure silyloxy homopolymer 1 is 78 °C, there is very little mixing between this polymer and the two small molecules (2, 4) examined in this study.

Phase separation would prevent interaction of the PAGs with the polymer and could suppress the hydrogen atom abstraction reaction which is necessary for acid production. The results obtained in the experiments described above indicate that it is vital to consider the miscibility of the PAG with the polymer matrix when considering their combination as a potential photoresist. To further explore the influence of polarity and miscibility, polymers containing both TMSS and TBS were examined by RBS.

Influence of [(*tert*-Butoxycarbonyl)oxy]styrene Incorporation on PAG Miscibility in Poly([(trimethylsilyl)oxy]styrene). For the 1:1 copolymer (6) of TMSS and TBS (Scheme 1) formulated with the arsenate PAG 2, there is an even distribution of silicon atoms throughout the polymer film before exposure (Table 1), but arsenic tends to segregate near the polymer/substrate interface. The arsenic concentration located in an ~1000-Å region adjacent to the silicon wafer surface is ~5 times greater than that in the top 6600 Å of the polymer film. Upon exposure and PEB, the film thickness decreases 4% and the distribution of arsenic in the film has not changed significantly: there is still a much higher concentration of arsenic-containing compounds in a 1000-Å region adjacent to the substrate surface. The concentration of silicon has decreased by ~20%. Some of the silyl ether groups have been cleaved, and the resulting hexamethyldisiloxane presumably has volatilized from the polymer film.

Using the less polar tosylate PAG 4 in conjunction with polymer 6 gives interesting results. The sulfur from the tosylate PAG is evenly distributed throughout the film both before and after exposure. Thus incorporation of TBS into the silyloxystyrene polymers increases mixing with the tosylate PAG 4. There is a 21% decrease in film thickness as well as a 47% relative reduction in the total number of silicon atoms upon exposure and PEB. The concentration of sulfur in the polymer film from the PAG, or the photogenerated acid, increases slightly. The increase in sulfur content simply reflects the change in film thickness and density of the material after exposure and PEB. As the polymer loses the *tert*-butoxycarbonyl (BOC) protecting groups, the film shrinks and the density of the film changes. Mathematical models have shown that the density of the deprotected polymer would be

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(9) Pierrat, C. AT&T Bell Laboratories, private communication.

Table 3

polym	% As[a]	% of total film thickness	% loss of Si[b]
1	100	6.2	0
7	86	19	2
6	44	13	17

[a] Percent of arsenic atoms in region adjacent to the silicon substrate prior to UV exposure. [b] After exposure and PEB.

higher than the density of the fully protected polymer.[9] The atomic percentages are calculated relative to the film density so that the percent of atoms remaining in the film may increase relative to the values given before exposure if the density of the film increases.

Incorporation of BOC groups into the silicon-bearing polymer alters the interaction between the PAGs and the polymer matrix. With a similar sulfur-containing PAG, approximately twice as much silicon was lost in the silyloxy homopolymer 1 (85%) than in the copolymer 6 (47%). These values are in approximate proportion to the amount of silicon bearing side groups in each material. That the silyl ether and BOC groups were cleaved in approximately equal amounts from copolymer 6 was confirmed by IR experiments. The intensities of the BOC carbonyl stretch (1759 cm^{-1}) and the silyl ether Si–O stretch (914 cm^{-1}) were calculated relative to the aryl C–C stretch of the polymer backbone. Approximately the same amount of BOC groups was cleaved (21%) as silyl ether groups (26%) upon exposure and PEB indicating that the photogenerated acid has an equal affinity toward cleaving either protecting group. In addition, sulfur atoms were lost from homopolymer 1 but not copolymer 6, suggesting that the PAG and/or the tosic acid photoproduct are miscible with the latter material. Tosic acid clearly is not miscible with homopolymer 1 and prefers to volatilize from the film.

Copolymers of TMSS and TBS in varying ratios (Scheme 1) were also investigated for resist solutions formulated with the arsenate PAG 2. Copolymer 7, which contains 75% of the [(trimethylsilyl)oxy]styrene monomer, behaves similarly to the silyl ether homopolymer 1 formulated with the same PAG. Before exposure, most of the arsenic atoms are confined to a 1500-Å region adjacent to the substrate surface (Table 1). After exposure and PEB, the distribution of arsenic in the film is identical to that found in the unexposed sample, and the silicon atom concentration decreased by less than 2%. The behavior of the polymer film changes dramatically as the amount of TMSS in the polymer is decreased. Copolymer 8 contains only 25% of the silyl ether monomer. With the arsenate PAG 2, the metal is evenly distributed throughout the film even prior to exposure (Table 1). Upon exposure and PEB, there is essentially no loss of film thickness, although the silicon atom concentration has decreased by 13% and the arsenic concentration remains unchanged.

The interaction between the arsenate 2 and these copolymers (6–8) changes dramatically with the polymer composition (Table 3). Only when the TBS composition in the polymer is in the range 50–75% does the arsenate PAG become miscible with the polymer matrix. Some of the results in Table 1 are summarized in Table 3. In homopolymer 1, 100% of the arsenic amount is located in a region that comprises less than 7% of the total film thickness. As more BOC groups are incorporated into the materials, the concentration of arsenic decreases in the region adjacent to the silicon substrate. Note that the amount of silicon atoms evolving from the polymer increases with increased incorporation of TBS. This is

Table 4. Compositional Characteristics of Selected Polymer/PAG Films

polym	PAG	exp	thickness (Å)	atomic % S	atomic % As
9	2	no	9100	0.027	0.023
		yes	8000	0.035	0.028
9	3	no	12,700	0.28	
		yes	10,800	0.28	
10	2	no	12300	1.24	0.052
		yes	10600	1.35	0.063
10	3	no	14500	1.30	
		yes	12400	1.43	
11	2	no	8680	0.055	0.034
		yes	8500	0.046	0.033
11	4	no	9450	0.30	
		yes	8400	0.34	
12	2	no	19000	0.060	0.035
		yes	17400	0.052	0.036

Scheme 4
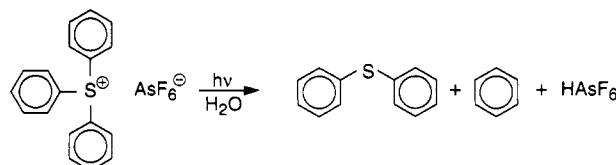
consistent with the proposal that the PAG is being more readily distributed throughout the polymer film. The precise TBS concentration at which this change in miscibility occurs has not been fully investigated.

Evaluation of Alternative Polymer Matrixes. Several other polymer systems (Scheme 1) were evaluated in conjunction with the PAGs described here in order to help understand the phenomenon of uneven PAG distribution. For the polymers not containing TMSS, the PAGs are consistently, uniformly distributed throughout the films both before, and after exposure and PEB. Results are shown in Table 4.

Use of the more polar hydroxystyrene (HS) monomer changes the region in which the silyl ether materials become miscible with typical PAGs. One example involves copolymer 5 which consists of [(trimethylsilyl)oxy]styrene and hydroxystyrene in a 1:1 ratio (Scheme 1). This copolymer should be significantly more polar than the equivalent TBS material 6 and thus should exhibit enhanced PAG solubility in comparison to its less polar, TBS, counterpart. In fact, when formulated with the arsenate PAG 2, the distribution of the PAG in a polymer film of 5 was found to be uniform.

Examination of the data in Table 4 reveals that the behavior of the arsenate PAG 2 was similar in polymers 9 (the TBS homopolymer) and 10 (a copolymer of TBS and SO₂). Specifically, the concentration of sulfur and arsenic atoms did not change with exposure and PEB. In contrast, for polymers 11 (a copolymer of TBS and HS) and 12 (a TBS/N-methylmaleimide copolymer), the atomic percent of sulfur decreased even though the arsenic concentration remained the same. Examination of the mechanism for acid generation from the arsenic containing onium salt, PAG 2 (Scheme 4), reveals that in addition to the formation of a protic acid, byproducts such as diphenyl sulfide are also produced. It would appear that the hexafluoroarsenic acid is nonvolatile and remains within the polymer matrix. The diphenyl sulfide byproduct is capable of volatilizing from the polymer matrices of 11 and 12 but not from 9 and 10. The polarity of the respective sets of polymers may explain this phenomenon. As

polymers 11 and 12 are much more polar than polymers 9 and 10, the nonpolar sulfide byproduct may be immiscible with the polar matrix, and thus volatilization of this small organic molecule readily occurs. Notably, neither the tosylate PAG nor its tosic acid photoproduct were seen to volatilize from films of polymers 6 and 9–12. This is demonstrated by the fact that the atomic percent of sulfur in these films did not change significantly upon exposure and PEB in the presence of the tosylate ester. In fact, the sulfur byproduct, tosic acid, remained in the films of all the polymers evaluated except for the silyloxy homopolymer 1. Tosic acid may be immiscible with this particularly nonpolar polymer (1) and thus may be more prone to sublime from the silicon-containing matrix.

Conclusion

Of the many systems examined, polymer 1 displayed the most unusual behavior with regard to miscibility, in particular with the arsenate PAG 2. Several factors may explain the nonuniform distribution of this small molecule in the polymer matrix. First, the nonpolar polymer 1 may tend to exclude the polar onium salt (2). Second, the hygroscopic arsenate PAG 2 may migrate to the polymer/substrate interface which is most likely to have the highest concentration of water and is therefore a polar surface. Third, the arsenate salt 2 is more soluble in the casting solvent than in the nonpolar polymer. During the spin-coating process, solvent evaporates from the air/polymer interface generating a polymer-rich, nonpolar surface. The concentration gradient may cause the dissolved arsenate salt to migrate toward the more polar region at the polymer/substrate interface. Fourth, the low surface tension of silicon may influence the distribution of PAG in the polymer matrix. Experiments with block copolymers containing siloxane segments suggest that the high surface density of silicon gives a polymer film with a silicon-rich polymer/air interface.[10] Overall, the highly polar arsenate salt may have limited solubility in the relatively hydrophobic polymer.

The tosylate PAGs are polar, non-ionic materials which lend themselves to improved miscibility with the polymers examined in this study. However, as noted above, even though the nitrobenzyl ester based PAGs are miscible, additional concerns arise once the acid is generated. Specifically, the highly polar acid may itself be immiscible. Under such circumstances, the acid may not be as efficient as it would be were it in a polar environment and as seen in the cases of polymer 1 and PAG 3, the acid may in fact volatilize from the matrix. From this information in conjunction with previous lithographic experiments,[1] we conclude that efficient photoresist systems should consist of polar PAGs and polar polymer matrices, as this maximizes interaction between the photogenerated acid and the polymer. Alternately, a nonpolar PAG in a nonpolar matrix may not be an ideal photoresist system. Clearly, the results from this study emphasize the need to carefully design a polymer material and its additives to effect the desired performance.

(10) Hartney, M. A.; Novembre, A. E.; Bates, F. S. *J. Vac. Sci. Technol.* 1985, *B3*, 1346.