Figure 4). No attempts were made to quantify carbon contamination using more sensitive techniques since the presence of excess antimony in the film and the poor morphology (granular in nature), as seen from visual inspection and Nomarski micrographs, indicated we had not optimized the deposition conditions. Nevertheless, the absence of carbon at the percent level in these films, together with the stability and volatility of the primary stibine, suggests it is a suitable candidate for further growth studies under more controlled conditions.

Conclusions:

From this study we have found that stable, volatile primary and secondary antimony hydrides can be synthesized in reasonably good yields. These compounds are significantly more stable and/or volatile than other organoantimony hydrides reported in the literature. This may be attributed to the presence of large organic substituents with no β-hydrogens. Our studies have also shown that these hydrides are transportable and can be used to deposit InSb. In particular, these compounds can be used with trimethylindium to deposit InSb at moderately low temperatures for organostibines (400 °C for $(Me_3CCH_2)_2SbH$ and 350 °C for $(Me_3CCH_2)SbH_2$). The primary stibine is extremely attractive because of its high volatility and low decomposition temperature, characteristics of interest in growing ternary antimonides or metastable antimonide-based materials.

Synthesis and Evaluation of Copolymers of (*tert*-Butoxycarbonyloxy)styrene and (2-Nitrobenzyl)styrene Sulfonates: Single-Component Chemically Amplified Deep-UV Imaging Materials

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Copolymers of (*tert*-butoxycarbonyloxy)styrene (*t*-BOC-styrene) and (2-nitrobenzyl)styrene sulfonates were prepared to give hydrophobic, photosensitive materials. Exposure to ultraviolet light converted the pendant 2-nitrobenzyl sulfonate esters to sulfonic acid moieties, and this photogenerated acid catalyzed the removal of the *t*-BOC groups on subsequent heating. The resulting material was a copolymer of 4-hydroxystyrene and styrenesulfonic acid, which was hydrophilic and soluble in aqueous base. Copolymers with different compositions (monomer ratios) and molecular weights were synthesized, and the resulting materials were analyzed by thermal and spectroscopic methods and evaluated for lithographic performance as positive tone resists. As the percentage of the photosensitive 2-nitrobenzylstyrene sulfonate monomer was increased, the lithographic sensitivity improved but the thermal stability of the copolymers decreased. The photoresponse of some of the materials was inhomogeneous, apparently the result of inhomogeneous distribution of acid-generating monomers in the polymers.

Introduction

The needs of the semiconductor industry continue to give impetus to the investigation of new chemistries for photoresists. These needs include the resolution of smaller features, improved sensitivity (or photospeed), and greater process latitude (the ability to tolerate more variation in processing conditions).[1] Chemically amplified deep UV photoresists are one promising class of materials for patterning in the submicron regime (0.25–1.0 μm).[2] Deep-UV is defined as light in the wavelength range 220–280 nm, though typically 248-nm KrF excimer laser radiation is employed. Chemical amplification refers to the increase in sensitivity achieved by harnessing the effect of each absorbed photon to catalytic resist chemistry.[3] A typical chemically amplified resist contains two components: a matrix polymer and a photoactive additive. Absorption of light by the photoactive compound generates the catalytic agent, usually a strong acid. Subsequent heating drives an acid-catalyzed chemical reaction of the matrix polymer, generally a deprotection or cross-linking reaction. The end result is different solubility properties for the exposed and unexposed areas of the resist film, allowing formation of the desired image.

A chemically amplified resist we have studied previously consists of poly[(*tert*-butoxycarbonyloxy)styrene-*co*-sulfur dioxide] (PTBSS) and a photoacid generator.[3d] We have

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Table I. Polymerization Conditions

copolym	feed ratio (TBS:NTS)	initiator[a]	temp, °C	copolym ratio[b] TBS:NTS	conversion g of polym/g of monom
8:1 HMW	19:1	0.065	67	8:1	0.26
11:1 HMW	30:1	0.065	67	11:1	0.28
9:1 LMW	22:1	0.061	68	9:1	0.44
14:1 LMW	35:1	0.050	68	14:1	0.35

[a]Relative to total monomers. [b]Determined by X-ray fluorescence.

Table II. Copolymer Properties

copolym	$\bar{M}_w$, D	MWD $\bar{M}_w/\bar{M}_n$	T_d, °C	T_g, °C	acid content, μmol/g
8:1 HMW	>1 200 000		128		57
11:1 HMW	>1 200 000		138	125	23
9:1 LMW	21 800	1.59	139	125	17
14:1 LMW	20 800	1.52	142	125	12

studied a number of photoacid-generating compounds, primarily 2-nitrobenzyl esters of sulfonic acids.[4] In the present study, we report the synthesis and preliminary evaluation of a one-component resist based on this previous work. This resist is a copolymer of (*tert*-butoxy-carbonyloxy)styrene (TBS) and [2-nitro-6-(trifluoro-methyl)benzyl]styrene sulfonate (NTS). Our previous studies[4] had shown that the 6-trifluoromethyl group was among the most effective in stabilizing 2-nitrobenzyl sulfonates with regard to thermal decomposition. Incorporation of both components into a single polymer was expected to provide several advantages, particularly improved homogeneity and diffusion control, which might improve the resolution capability. There have been several reports of one component resist systems in the past, some of which employed chemical amplification.[5]

Results and Discussion

Synthesis and Thermal Properties. NTS was synthesized by condensation of 4-(chlorosulfonyl)styrene[6] with 2-nitro-6-(trifluoromethyl)benzyl alcohol in the presence of triethylamine and purified by recrystallization from toluene. TBS was obtained from Eastman Kodak. Copolymers were produced by free radical polymerization in toluene with benzoyl peroxide as the thermal initiator. Nitro aromatics such as NTS are known to be free radical scavengers,[7] and a light brown color in the crude mixtures following polymerization was evidence of some decomposition. Four TBS/NTS copolymers were prepared, with different molecular weights and compositions. The polymerization conditions which resulted in these copolymers are summarized in Table I and detailed in the Experimental Section. The physical properties of the materials are summarized in Table II. Molecular weights were determined by high-pressure size exclusion chromatography (HPSEC). The high molecular weight copolymers were prepared with minimal toluene solvent, nearly under bulk conditions, and had $\bar{M}_w$ values greater than the res-

olution limit of the HPSEC columns (1 200 000). The low molecular weight copolymers were prepared at moderate dilutions and had measured $\bar{M}_w$ values near 20 000. Feed ratios of TBS:NTS of approximately 20:1 and 30:1 were used for both molecular weight regimes. X-ray fluorescence was used to determine the actual TBS:NTS ratios. The measured sulfur in the copolymers ranged from 1.66 to 0.96 wt%, corresponding to TBS:NTS ratios from 8:1 to 14:1. The four copolymers are designated descriptively as 8:1 HMW, 9:1 LMW, 11:1 HMW, and 14:1 LMW. The numbers indicate the experimentally measured TBS:NTS ratio, and the acronym indicates high or low molecular weight. The proportionally greater incorporation of the styrene sulfonate monomer into the copolymers reveals that NTS is more reactive than TBS under the polymerization conditions. An approximate calculation of the reactivity ratios can be made from the data in Table I. (A rigorous study of reactivity ratios would require more data and low conversions (<5%).[8] If NTS is considered to be monomer 1 and TBS to be monomer 2, then r_1 and r_2 are calculated to be 5 and 0.3, respectively.

Thermal Analysis. Thermogravimetric analysis (TGA) of TBS-based polymers generally shows one major weight loss event between 100 and 200 °C, corresponding to the thermal decomposition of the *tert*-butoxycarbonyloxy (*t*-BOC) protecting groups, with loss of carbon dioxide and isobutylene. For the homopolymer of TBS, the onset temperature for decomposition (T_d) is 188 °C, while for PTBSS copolymers T_d ranges from 150 to 180 °C, depending on the composition and molecular weight.[9] The T_d of TBS/NTS copolymers was also found to correlate with composition and molecular weight. The observed T_d values can be found in Table II. A lower rate of TBS:NTS (that is, more NTS in the copolymer) led to a lower T_d, and a higher molecular weight also led to a lower T_d. Differential scanning calorimetry (DSC) of the copolymers revealed glass transition temperatures (T_g) essentially identical to that of poly-TBS (125 °C). The measured T_d values for the TBS/NTS copolymers are considerably lower than the T_d of poly-TBS, and since low decomposition temperatures are deleterious to the performance of these materials as resists, the cause of the low T_d values was sought. The decomposition temperature of the NTS monomer was measured by DSC and found to be 200 °C. This indicated that thermal acid generation from NTS in the copolymers was not likely to occur in the temperature range of the observed T_d values (120–150 °C). The primary source of the low T_d values was discovered to be the presence of acidic impurities in the copolymers. A spectroscopic technique was used to quantitate the amount of these impurities in the different copolymers. A calibration curve was generated by adding known amounts of strong mineral acid (HCl) to standard samples of the acid–base indicator bromophenol blue and then measuring the absorbance at 610 nm.[10] The absorbance of standard samples of the indicator to which 1.0 mg portions of the co-

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(8) The reactivity ratios r_1 and r_2 are defined as ratios of rate constants, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. These rate constants describe the rate of reaction of a certain monomer with a living chain end formed by another monomer. So k_{12} is the rate of reaction of monomer 1 with a chain whose living terminus is a unit of monomer 2, and so on. A detailed discussion can be found in Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley and Sons: New York, 1981.

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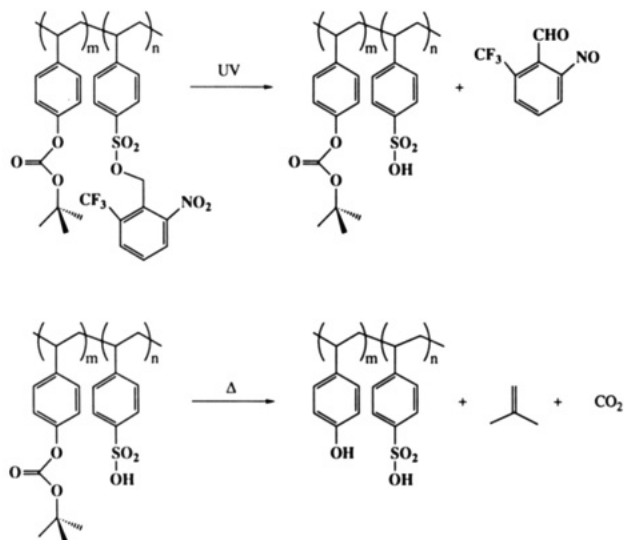
Figure 1. Resist chemistry of TBS/NTS copolymers.

Table III. Sensitivity and Contrast of Copolymers[a]

	TMAH Developer		isopropyl alcohol developer	
material	D_s, mJ	γ	D_s, mJ	γ
tosylate[b]	90	6.5		
8:1 HMW	130	6.7		
11:1 HMW	420	1.5	120	7.6
9:1 LMW	470	1.8	200	3.3
14:1 LMW	450	1.2	245	2.5

[a] See text for conditions. [b] 2-Nitro-6-(trifluoromethyl)benzyl-toluene sulfonate at 10 mol % in poly-TBS.

polymers had been added were compared to the calibration curve to determine the acid content of the copolymers. These acid contents ranged from 10 to 60 μmol/g of polymer. The actual values are listed in Table II and can be seen to correlate with the observed T_d values. Samples of TBS homopolymer and NTS monomer were found to have no detectable acid. Acidic impurities could form by hydrolysis of NTS or by its radical induced decomposition during polymerization. Since the monomer is free of acid and evidence of decomposition is observed during polymerization (vide supra), we believe radical decomposition is the source of the acidic impurities.

Lithographic Evaluation. The resist chemistry of the TBS/NTS copolymers is shown in Figure 1. Irradiation with deep UV light induces a rearrangement of the NTS groups, resulting in styrenesulfonic acid as part of the polymer chain with 2-nitroso-6-(trifluoromethyl)benz-aldehyde as a side product. On subsequent heating (the postexposure bake), the photogenerated acid catalyzes the deprotection reaction of the TBS groups. The end result is a copolymer of styrenesulfonic acid and 4-hydroxy-styrene, which is soluble in aqueous base. The TBS/NTS copolymers are insoluble in base, giving positive tone images with aqueous base development. The lithographic response (sensitivity and contrast) of the copolymers was evaluated using proximity printing exposures through a variable density mask with a KrF excimer laser as the light source. A 75-s bake at 120 °C followed the exposure, and both 0.17 N tetramethylammonium hydroxide (TMAH) and isopropyl alcohol were employed as developers. The clearing doses (D_s) for large areas and the contrast parameter, γ, are listed in Table III.[11] With TMAH de-
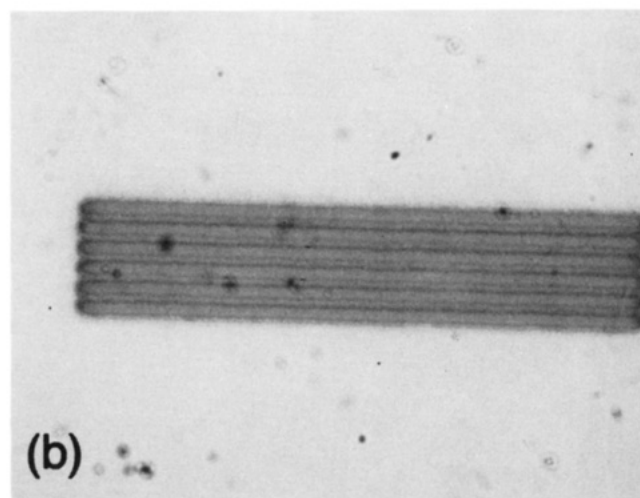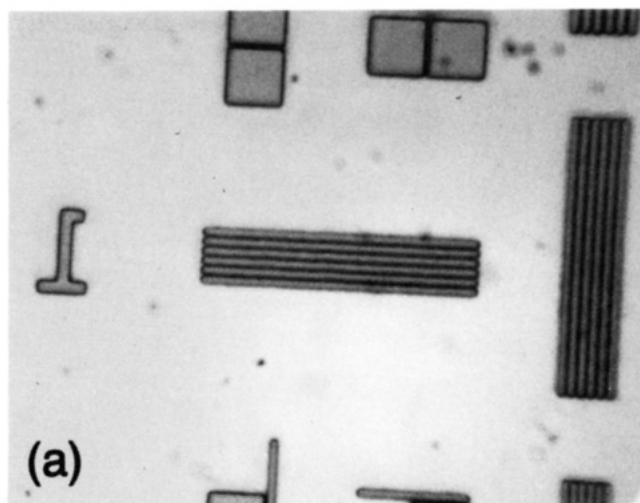

Figure 2. 1.0-μm lines and spaces in the 11:1 HMW copolymer: (a) 80×; (b) 160×.

velopment the 8:1 HMW copolymer was considerably more sensitive and had higher contrast than the other copolymers. The improved sensitivity is partially due to thermal deprotection of this material during the postexposure bake. Chemically amplified resists usually show high contrast, and the other copolymers are unusual in this respect. This low contrast was more easily understood in light of the results of infrared (IR) studies of the polymers (vide infra). Comparison with 2-nitro-6-(trifluoromethyl)benzyl-p-toluenesulfonate, a small-molecule acid generator studied previously,[4] revealed that the processing conditions are capable of a sensitivity below 100 mJ/cm². These data are also included in Table III. Isopropyl alcohol as a developer is more tolerant of incomplete deprotection. Isopropyl alcohol development gave better results, as listed in Table III, with the exception of the 8:1 HMW copolymer. This material proved to be soluble in isopropyl alcohol even in the unexposed areas, probably due to thermal deprotection.

Line and space patterns down to 1.0 μm were resolved in the copolymers using vacuum contact printing. The best results were obtained in the 11:1 HMW copolymer and are shown in Figure 2. The 8:1 HMW copolymer exhibits low

(11) The sensitivity parameter D_s and contrast parameter γ are defined in: Thompson, L. F.; Bowden, M. J. In *Introduction to Microlithography*; ACS Symposium Series No. 219; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.: American Chemical Society: Washington, D.C., 1983; pp 161–215.
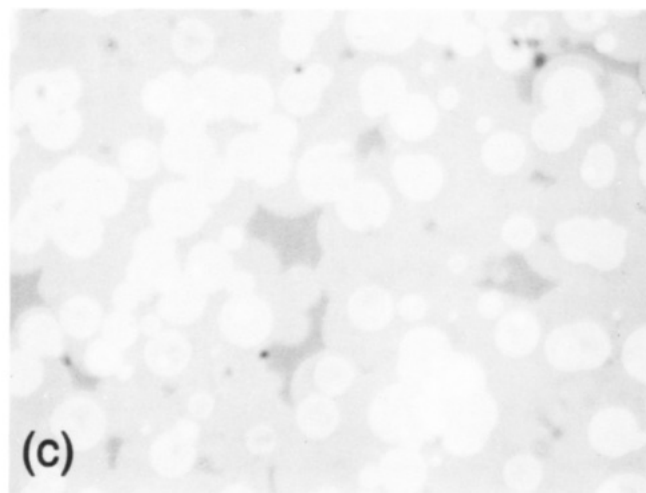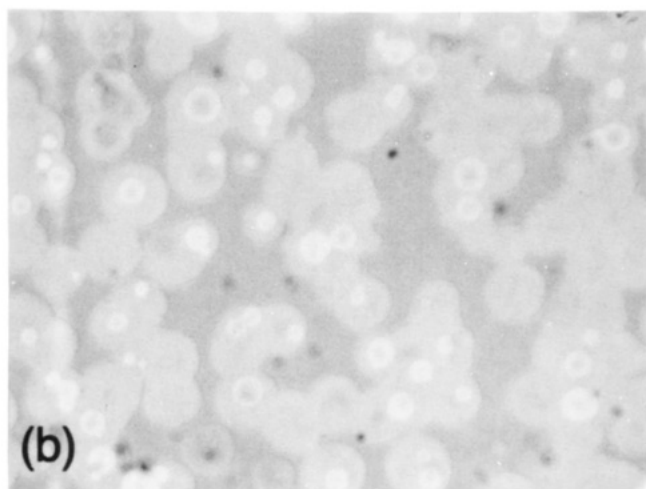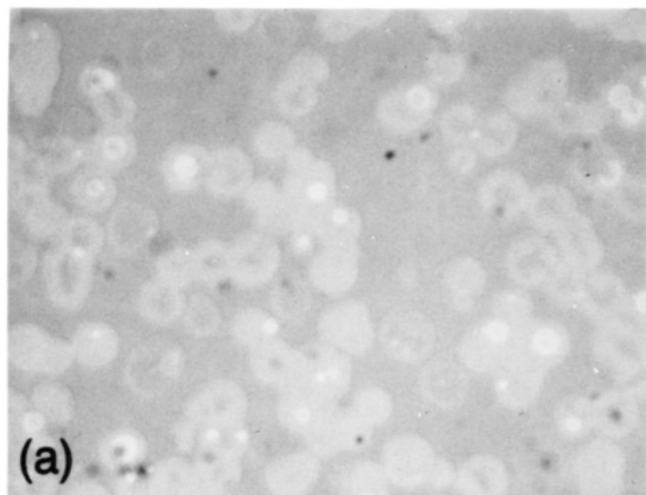
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(a)

(b)

(c)

Figure 3. Inhomogeneous development in the 14:1 LMW copolymer at 50×: (a) 120 mJ/cm², (b) 150 mJ/cm², (c) 180 mJ/cm². The thickness of the film can be judged approximately by its darkness, with the darker areas being thicker than the lighter areas. (The shades actually correspond to different interference colors in the film.)

thermal stability and this appeared to decrease resolution performance. The 9:1 and 14:1 LMW copolymers tended to develop inhomogeneously, with deprotection (as measured by film thickness) beginning in certain areas and spreading out until those areas merged. Figure 3 shows this inhomogeneous development in the 14:1 LMW copolymer.
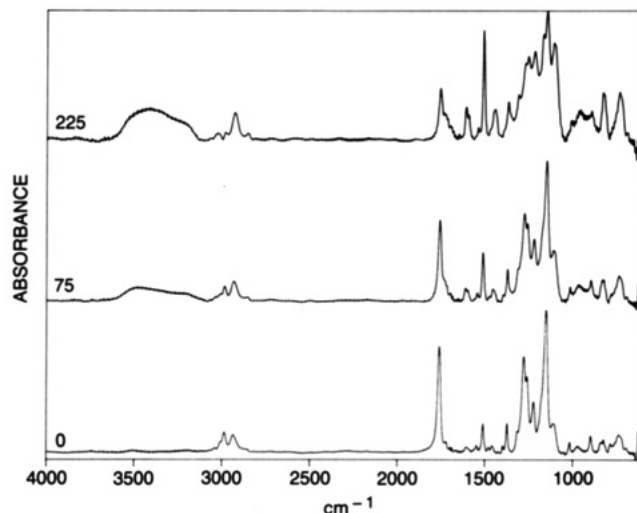

Figure 4. Infrared spectra of the 9:1 LMW copolymer after exposure to 0, 75, and 225 mJ/cm² of 248-nm radiation followed by a 75-s, 120 °C bake.

Table IV. Percent *t*-BOC Remaining[a] after Exposure and Postexposure Bake (120 °C, 75 s)

dose, mJ/cm²	8:1 HMW	11:1 HMW	9:1 LMW	14:1 LMW
0	0.30	0.68	1.00	1.00
75	0.14	0.38	0.60	0.42
150	0.13	0.22	0.42	0.27
225	0.11	0.19	0.32	0.23
300	0.11	0.18	0.27	0.19

[a] Determined by IR.

Infrared Analysis. Infrared (IR) spectroscopy has proven useful in understanding the chemistry of chemically amplified photoresists based on TBS.[12] Generally 90–95% of the *t*-BOC protecting groups must be removed before the polymer becomes aqueous base soluble. The conversion of *t*-BOC styrene to hydroxystyrene can be followed by observing the reduction in area of the carbonyl band in the IR spectra of exposed and baked films. Figure 4 demonstrates the effect of exposure to 248-nm radiation followed by baking, on the IR spectra of the 9:1 LMW copolymer. An ∼0.5-μm-thick film of this copolymer was spun onto a double-polished silicon substrate. Different sections of the films were exposed to different amounts of radiation, after which the film was baked at 120 °C for 75 s. Exposure doses of 0, 75, and 225 mJ/cm² are shown in Figure 4. It can be seen that increasing exposure leads to increased deprotection, as measured by the decrease in the carbonyl band at 1760 cm⁻¹ and the increase in the hydroxyl band at 3500 cm⁻¹. The amount of deprotection can be calculated by normalizing the integrated area of the carbonyl band to the area of the band at 825 cm⁻¹. This band appears to be from the silicon substrate and is unaffected by the deprotection reaction. Table IV lists the percent *t*-BOC remaining as a function of exposure dose for the four copolymers. The high molecular weight copolymers exhibit some thermal deprotection from the postexposure bake, so they are not fully protected even with no UV exposure. The postexposure bake conditions also affect the extent of deprotection. Figure 5 shows spectra of the 14:1 LMW copolymer after exposure to 150

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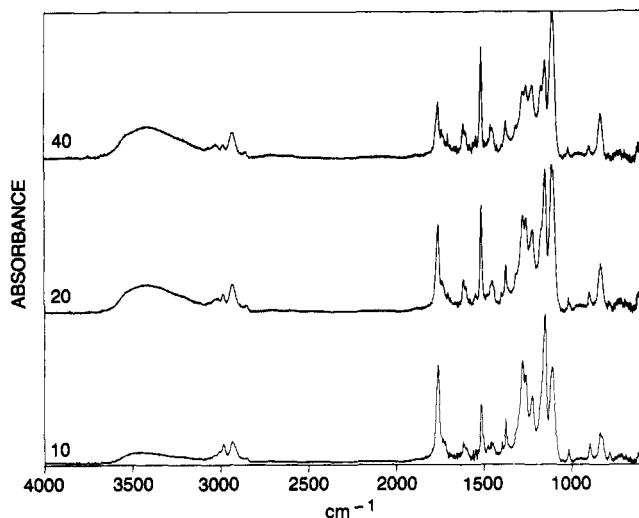
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Figure 5. Infrared spectra of the 14:1 LMW copolymer after exposure to 150 mJ/cm^2 of 248-nm radiation followed by 10-, 20-, and 40-s, 125 °C bake.

mJ/cm^2 of 248-nm light followed by postexposure bakes of 10, 20, and 40 s at 125 °C. Increasing the bake time increases the extent of deprotection. The data in Table IV suggest that there is a limit to the amount of deprotection that occurs with increasing dose. For the high-ratio copolymers (14:1 LMW and 11:1 HMW) the extent of t-BOC removal appears to level off at approximately 80% deprotection, while deprotection of the 8:1 HMW copolymer levels off around 90%. A similar saturation effect can be observed with increasing post-exposure bake time.

These observations, along with the fact that 300 mJ/cm^2 exposures fail to completely deprotect some of the copolymers (when previous studies with small-molecule 2-nitrobenzyl sulfonates suggest that deprotection should be complete below 200 mJ/cm^2),[4] imply that there are regions of the film where the t-BOC groups are outside the diffusion radius of any photogenerated acid.[13] To address this question, a simple calculation of the distribution of acid functional groups in the copolymers was performed. Assuming a density of 1 g/cm^3, a cubic micron of a 14:1 copolymer should contain 1.7×10^8 styrenesulfonate esters. While the quantum yield of 2-nitrobenzyl ester rearrangements may exceed 0.5 in solution, incorporation into a polymer matrix lowers the quantum yield significantly, usually to between 0.05 and 0.1.[14] Measurements of quantum yields on the copolymers gave values between 0.03 and 0.09. The 14:1 LMW copolymer had a measured quantum yield of 0.06 and an absorbance of 0.32 for a 1.0 μm film at 248 nm. A dose of 300 mJ/cm^2 should generate 1×10^7 sulfonic acid groups in a cubic micron. If these were evenly distributed, each would need to clear a cubic volume 46 Å on each side. With a density of 1 g/cm^3, this volume would contain approximately 250 t-BOC styrene side chains. Catalytic chain length measurements have shown that over 1000 turnovers for each acid equivalent are possible.[4,10] The acid generated by 300 mJ/cm^2 of DUV light should therefore easily remove all of the t-BOC groups, even in the 14:1 LMW copolymer. However, the sulfonic acid groups are almost certainly *not* evenly dis-

tributed in the copolymer. The reactivity ratios reported above would tend to concentrate the styrene sulfonate monomers in those sections of polymer chains which formed early in the polymerization. In fact, a 35% yield of a 14:1 copolymer from a starting monomer ratio of 35:1 requires that over 75% of the styrene sulfonate is incorporated into the copolymer. Regions of polymer chains formed late in the polymerization (including entire chains *initiated* late in the polymerization) will be depleted in photoacid generating monomer. This may result in some t-BOC groups in the film which are too distant from any sulfonic acid group for acid catalysis of the deprotection reaction to be effective. There may also be some incompatibility between the "early" polymer (which will contain many fluorinated styrene sulfonate esters) and "late" polymer (which will be mostly t-BOC-styrene). While macroscopic phase separation was not observed, microphase separation may be occurring. The fluorine-rich sections of polymer may be self-associating while remaining dissolved in the predominantly hydrocarbon polymer. The observation that inhomogeneous deprotection radiates out from "centers" where acid is generated (Figure 3) is consistent with this concept. This will result in a lower sensitivity when the material is employed as a resist.

Conclusions

These studies on copolymers of TBS with 2-nitrobenzylstyrenesulfonate esters demonstrate that such materials have potential as one-component deep-UV photoresists. The materials described here are not practical due to their low sensitivities and thermal stabilities, but the observation of inhomogeneities apparently due to inhomogeneous distribution of acid suggests that restriction of acid diffusion could be used to advantage in gaining resolution. Several issues remain to be addressed for these materials. First, the synthetic procedure must be modified to eliminate the acidic impurities which lead to low thermal stabilities. This could be achieved by modifying the polymerization conditions or by changing to a more stable photoacid-generating monomer. Second, the copolymers are not random but have an inhomogeneous distribution of acid generating monomers. This results in low sensitivity and contrast. Continuous addition of the more reactive monomer to maintain a constant ratio of monomer concentrations should solve this problem. Third, the T_g values of the copolymers need to be raised. This could be accomplished by terpolymerization with sulfur dioxide.[7] One component systems such as the TBS/NTS copolymers described here appear to be viable as photoresist materials, with particular applications at high resolution.

Experimental Section

All chemicals were used as received from commercial vendors with the exception of toluene used as a polymerization solvent, which was distilled from calcium hydride. Proton NMR spectra were obtained on a General Electric QE-300 FT-NMR, and are reported in ppm downfield from tetramethylsilane. Electronic (UV–visible) spectra were taken on a Hewlett-Packard 8452A diode array spectrometer. Infrared spectra were recorded on a Mattson Galaxy 8020 Fourier transform infrared spectrometer, and peak positions are reported in wavenumbers (cm^{-1}). Mass spectra were obtained on a Hewlett-Packard 5989A mass spectrometer in electron-impact mode, coupled with a Hewlett-Packard 59980B particle beam and a Hewlett-Packard liquid chromatography system.

4-Styrenesulfonyl Chloride.[6] Dimethylformamide (80 mL) was cooled to 0 °C under N$_2$ in a 250-mL round-bottom flask. Thionyl chloride (50 mL) was added, and the mixture stirred at 0 °C for 30 min. Sodium 4-styrenesulfonate (16.1 g, 78.3 mmol) was added in small portions. The mixture was stirred for 10 h,

(13) It is also possible that sulfonate esters, which have not photochemically rearranged to the acid, are helping to make the resist base insoluble at low doses. This does not explain the IR results, however.

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allowed to warm to room temperature, and then placed in the refrigerator for 36 h. The mixture was then poured cautiously onto 300 mL of crushed ice and then extracted with toluene (3 × 100 mL). The combined organics were washed with saturated NaCl (100 mL) and dried (Na$_2$SO$_4$). The drying agent was removed by filtration and the solvent removed in vacuo. Distillation at reduced pressure (bp 82 °C, 0.01 mmHg) gave 8.5 g (42.0 mmol, 53% yield) of 4-styrenesulfonyl chloride as a clear liquid. NMR (CDCl$_3$) 5.51 (d, 1 H), 5.98 (d, 1 H), 6.72 (d of d, 1 H), 7.60 (d, 2 H), 7.96 (d, 2 H).

2-Nitro-6-(trifluoromethyl)styrene-4-sulfonate (NTS). 4-Styrenesulfonyl chloride (3.40 g, 16.8 mmol) and 2-nitro-6-(trifluoromethyl)benzyl alcohol (3.51 g, 15.9 mmol) were dissolved in 80 mL of toluene. Triethylamine (2.2 mL, 1.60 g, 15.8 mmol) was added via syringe. The mixture was stirred in the dark for 17 h, then the triethylammonium chloride was removed by filtration, and the solvent was removed in vacuo. Recrystallization from chloroform/cyclohexane gave 5.1 g (12.8 mmol, 80% yield) of 2-nitro-6-(trifluoromethyl)styrene-4-sulfonate as white crystals, mp 91–93 °C. NMR (CDCl$_3$) 5.44 (s, 2 H), 5.48 (d, 1 H), 5.94 (d, 1 H), 6.74 (d of d, 1 H), 7.56 (d, 2 H), 7.67 (t, 1 H), 7.83 (d, 2 H), 7.95 (d, 1 H), 7.98 (d, 1 H). IR (KBr) 3094, 2897, 1597, 1543, 1465, 1370, 1315, 1209, 1175, 1123, 1098, 961, 845, 820, 774, 740, 665. MS *m/e* 387 (M$^+$).

Polymerizations. *8:1 HMW.* In a vacuum flask, 0.880 g (2.3 mmol) of NTS, 10 g (45 mmol) of TBS, and 0.75 g (3.0 mmol) of BPO were dissolved in 50 mL of freshly distilled toluene. The mixture was degassed by extensive pumping (2–3 h) on a vacuum line, which also served to remove most of the solvent. The mixture was then stirred at 67 °C for 16 h. The polymer was recovered by dropping the resulting viscous, brown solution into 1 L of petroleum ether, and purified by dissolving in tetrahydrofuran and reprecipitating from petroleum ether. The yield was 2.8 g (26%), and the sulfur content was 1.65% (wt %) by X-ray fluorescence. Size exclusion chromatography gave $\bar{M}_w$ >1 200 000.

11:1 HMW. The procedure for the 8:1 HMW copolymer was used, except the reactants were 0.587 g (1.5 mmol) of NTS, 10 g (45 mmol) of TBS, and 0.75 g (3.0 mmol) of BPO. The yield was 3.0 g (28%), the sulfur content was 1.14%, and size exclusion chromatography gave $\bar{M}_w$ >1 200 000.

9:1 LMW. In a vacuum flask, 0.768 g (2.0 mmol) of NTS, 9.6 (43.5 mmol) of TBS, and 0.71 g (2.9 mmol) of BPO were dissolved in 50 mL of freshly distilled toluene. The mixture was degassed by extensive pumping on a vacuum line, which also served to remove most of the solvent. Just before polymerization was initiated, an additional 10 mL of toluene was introduced via syringe and pumping resumed for 5 min. The mixture was then stirred at 68 °C for 18 h. The polymer was recovered by dropping the resulting viscous, pale brown solution into 1 L of petroleum ether and purified by dissolving in tetrahydrofuran and reprecipitating in petroleum ether. The yield was 4.5 g (43.5%), with a sulfur content of 1.3%. Size exclusion chromatography gave $\bar{M}_w$ = 21 800 and a dispersity ($\bar{M}_w/\bar{M}_n$) of 1.59.

14:1 LMW. The procedure for the 9:1 LMW copolymer was used, except the reactants were 0.504 g (1.3 mmol) of NTS, 9.9 g (45 mmol) of TBS, and 0.55 g (2.3 mmol) of BPO. The yield was 3.70 g (35%), the sulfur content was 0.96%, and size exclusion chromatography gave $\bar{M}_w$ = 20 800 and $\bar{M}_w/\bar{M}_n$ = 1.52.

Thermal Analysis. Thermogravimetric analysis and differential scanning calorimetry were performed on a Perkin-Elmer-TGS-7 thermogravimetric analyzer or DSC-4 differential scanning calorimeter. The temperature scanning rate was 10 °C/min, and sample sizes were normally 2.5 mg.

Infrared Analysis. Infrared spectra were acquired on a Mattson Instruments Galaxy 8020 FTIR spectrophotometer operating in the single-beam mode. Polymers were spin-coated out of cyclo-

hexanone onto double-polished silicon substrates and prebaked at 105 °C for 90 s to remove excess solvent. The wafers were then exposed as required and baked at 120–125 °C to accomplish deprotection. Mattson Instruments' FIRST software was used to integrate peak areas for quantitative analysis. To determine the extent of deprotection, a band at 825 cm^{-1} (apparently due to the substrate itself) was used as a standard, since some of the polymers underwent deprotection in unexposed areas during the postbake. The 825-cm^{-1} band was a constant for any given substrate.

Lithographic Analysis. For lithographic analysis, 10% weight/volume solutions of the copolymers were prepared in cyclohexanone and filtered through 0.2-μm filters. Silicon wafers were vapor primed with hexamethyldisilazene and spin-coated with 0.5–1.0-μm films of the copolymers. The wafers were prebaked on a hot plate with a vacuum hold-down chuck at 120 °C for 60–75 seconds to remove the excess solvent. Exposures were performed on a Süss contact aligner (Model MA-56A) equipped with a Lambda-Physik KrF excimer laser as the light source. Proximity printing was used to generate sensitivity curves, and vacuum contact printing was used for resolution studies. Postexposure bake on a hot plate at 120 °C for 75 s followed by immersion development (isopropanol or 15:1 H$_2$O to 25% tetramethylammonium hydroxide in H$_2$O) for 60 s and a 60-s H$_2$O rinse was the standard process. Film thickness was measured on a Nanospec film thickness gauge (Nanometrics, Inc.).

Analysis for Acidic Impurities. A stock solution of bromophenol blue sodium salt in cyclohexanone was made so that the absorbance at 610 nm approximately 0.6. Aliquots of this solution (5 mL) were treated with 0–100 μL of 0.001 N HCl in methanol. The absorbance at 610 μm was measured to generate a calibration curve. The acid content of the copolymers was obtained by adding a 1.0-mg sample to 5 mL of the stock solution and measuring the absorbance at 610 μm after mixing thoroughly. Comparison to the calibration curve gave the amount of acidic impurities.

Quantum Yield Experiments. A calibration curve for the absorbance of bromophenol blue at 160 nm was prepared as described above. Silicon wafers were coated with 0.5–1.0 μm of the copolymers by spin-coating from cyclohexanone, and baked at 105 °C for 90 s. The wafers were then split in half, and one half was exposed to 150 mJ/cm^2 of 248-nm light. The resist was then removed from the wafers with a razor blade and placed in a tared vial. A standard aliquot of the bromophenol blue stock solution was added to the known mass of polymer, and the absorbance measured at 610 nm. The amount of acid in the exposed and unexposed polymer was determined from the calibration curve. The absorbance of the polymers at 248 nm was determined by spinning films onto quartz disks and measuring the absorbance and thickness. From the known values of absorbance/μm and amount of acid generated from a given dose, the quantum yield of acid generation could be determined. The quantum yields were 0.04 for the 8:1 HMW copolymer, 0.03 for the 11:1 HMW copolymer, 0.09 for the 9:1 LMW copolymer, and 0.06 for the 14:1 LMW copolymer.