Positive, Chemically Amplified Aromatic Methacrylate Resist Employing the Tetrahydropyranyl Protecting Group

Gary N. Taylor,* Larry E. Stillwagon, and Francis M. Houlihan

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Thomas M. Wolf

AT&T Bell Laboratories, Allentown, Pennsylvania 18103

Dotsevi Y. Sogah[†] and Walter R. Hertler

Du Pont Company, Central Research and Development,[‡] Experimental Station, Wilmington, Delaware 19880-0328

Received April 15, 1991. Revised Manuscript Received September 4, 1991

In this paper we describe the synthesis, properties and lithographic behavior of a new class of chemically amplified, positive-tone, aromatic methacrylate resists incorporating the tetrahydropyranyl protecting group bound to base-solubilizing carboxylic acid moieties. Copolymers containing equimolar amounts of benzyl methacrylate and tetrahydropyranyl methacrylate were prepared by free-radical and group-transfer polymerization (GTP). Photogenerated sulfonic acids formed from covalent ester or ionic salt precursors were used to remove the acid-labile tetrahydropyranyl (THP) group by heating after exposure. The resulting copolymers of benzyl methacrylate (BMA) and methacrylic acid (MAA) are extremely soluble in aqueous base solutions when the MAA concentration exceeds 35 mol %, thus affording positive tone patterns. This class of resins has low absorbance at 248 nm needed for patterning ≥1-μm-thick films. The moderate THP group concentration and its relatively small size minimize shrinkage during thermal and plasma processing. The nearly monodisperse polymers formed by GTP offer the advantages of better molecular weight control and the opportunity to study the effect of molecular weight distribution on this class of resists. We have studied these copolymer resists and find them to have high sensitivity (<30 mJ/cm^2) when formulated with aromatic sulfonate or trifluoromethyl sulfonate sensitizers. Contrast is greater than 2, and submicrometer patterns in 1-μm-thick films are resolved. Resolution is significantly influenced by the sensitizer, postexposure heating, and development conditions. Resolution presently is limited by resist adhesion which remains to be optimized. Plasma etching resistance to conditions used to etch Al is 1.8 times less than for hard-baked HPR-206 photoresist but can be improved to a value of 1.5 by postexposure thermolysis. Improvements are needed before this type of chemically-amplified resist is able to meet all deep-UV lithographic requirements.

Introduction

In this paper we describe a new class of positive, base-soluble chemically amplified[1] deep-UV resists. Two recent conferences[2,3] were devoted to discussing chemical amplification materials and technology. This intense interest underscores the importance of chemically amplified resists since they are the only resist class having sufficient sensitivity for use with the excimer laser stepper[4] and scanning[5] deep-UV exposure tools which have low fluences of deep-UV radiation.

Since its inception,[1] many approaches to chemically amplified positive resists have been reported. Most employ the photolytic generation of strong acids which, in turn, catalyze thermal reactions that enhance the solubility of the exposed region (Figure 1). A wide variety of polymer resins, acid labile groups, and photoactive acid generators have been studied. Base-soluble resins based on the polystyrene structure have been preferred due to their good etching resistance and low deep-UV absorbance. Positive resists have mainly employed the base-soluble phenolic group protected by *tert*-butoxycarbonyl[6] and tetrahydropyranyl[7] moieties which are very labile in the presence of strong acid.

A considerable number of photoacid generators also have been tested including a number of aromatic onium salts having both inorganic and organic counterions,[8] covalent organic materials such as the (halomethyl)triazines[9] and the nitrobenzyl esters of various fluoroaliphatic and aromatic sulfonic acids.[10] Intensive studies of the chemical, structural, and compositional aspects and the intricate processing needed to produce high-resolution patterns in thick (1 μm) films have brought considerable success.[11,12] However, a number of factors still remain to be investigated and are little understood.

[†] Present address: Department of Chemistry, Cornell University, Ithaca, NY 14853-1301.

[‡] Contribution no. 7531.

(1) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012.

(2) Symposium, on "Photoacid Generating Compounds: Chemistry and Applications to Polymeric Materials"; Proc. ACS Div. of Polymeric Materials: Science and Engineering, Vol 61, American Chemical Society Meeting, Miami Beach, FL, Sept 11-12, 1989.

(3) International Symposium on "Chemical Amplification Resists for Microlithography"; Tech. Assoc. of Photopolymers Japan, June 20, 21, 1990; *J. Photopolym. Sci. Technol.* **1990**, *3*, 219-422.

(4) Pol, V.; Bennewitz, J. H.; Esher, G. C.; Feldman, M.; Firtion, V. A.; Jewell, T. E.; Wilcomb, B. E.; Clemens, J. T. *Proc. SPIE* **1986**, *633*, 6.

(5) Buckley, J. D.; Karatzas, C. *Proc. SPIE* **1989**, *1088*, 424.

(6) Ito, H.; Willson, C. G. Proc. Reg. Tech. Conf. Soc. Plast. Eng., Mid-Hudson Sect., Ellenville, NY, Nov 8-10, 1982; pp 333-335.

(7) Hayashi, N.; Hesp, S. M. A.; Ueno, T.; Toriumi, M.; Nonogaki, S. Proc. ACS Div. Polym. Materials: Sci. and Eng.; American Chemical Society Meeting, Miami Beach, FL, Sept 11-12, 1989; Vol. 61, pp 417-421.

(8) Crivello, J. V.; Conlon, D. A.; Lee, J. L. In ref 7, Vol. 61, pp 422-426.

(9) Berry, A. K.; Feely, W. E.; Thompson, S. D.; Calabrese, G. S.; Sinta, R.; Lamola, A. A.; Thackeray, J. W.; Orsula, G. W. *Proc. SPIE* **1990**, *1262*, 575 and references therein.

(10) Houlihan, F. M.; Reichmanis, E.; Thompson, L. F.; Tarascon, R. ACS Symp. Series 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington D.C., 1989; pp 39-56.

(11) Maltabes, J. G.; Holmes, S. J.; Morrow, J. R.; Barr, R. L.; Hakey, M.; Reynolds, G.; Brunsvold, W. R., Willson, C. G.; Clecak, N.; MacDonald, S. A.; Ito, H. *Proc. SPIE* **1990**, *1262*, 2.

(12) Nalamasu, O.; Cheng, M.; Kometani, J. M.; Vaidya, S.; Reichmanis, E.; Thompson, L. F. *Proc. SPIE* **1990**, *1262*, 32.

0897-4756/91/2803-1031$02.50/0

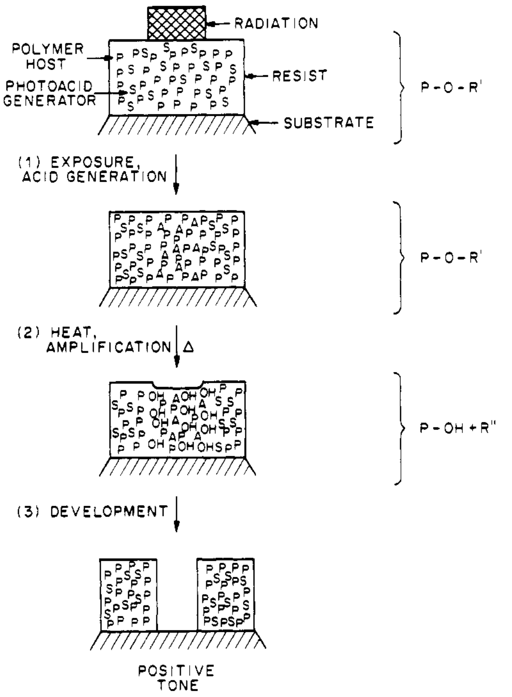
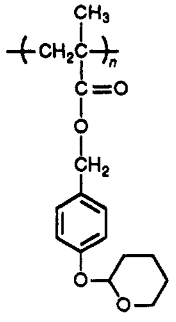


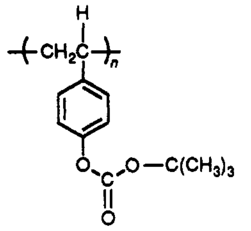
Figure 1. Scheme outlining the chemical amplification process in resist patterning where P-O-R' denotes a reactive polymer group, S is a photosensitive acid generator, A the acid generated photolytically, and OH is a base soluble group on the polymer. The smaller volume in the exposed region after step 2 results when volatile product R'' is expelled.

We address some of these issues in this paper using protected, normally base-soluble aromatic methacrylate polymers as the resin component. A few reports of this resin class in resist formulations have appeared.[13,14] We have investigated other low-absorbance materials in this polymer class and note our reasons for selecting them. First, the incorporation of aromatic groups on the acrylic polymer ester side chain confers a considerable degree of plasma stability to the normally very fragile acrylate and methacrylate backbones.[14] Binding the aromatic moiety to the ester group via suitable aliphatic spacer groups provides the low absorbance required for deep-UV exposure, whereas direct binding, via the phenyl esters, affords unacceptably high absorption.[13] Such structures also are compatible with facile monomer synthesis and easy preparation of low-to-high molecular weight polydisperse polymers by conventional free-radical polymerization[16] and low-to-moderate molecular weight monodisperse methacrylate polymers by the group-transfer polymerization (GTP) method.[17] With methacrylates, mono- and polydisperse polymers of equivalent molecular weight can be readily prepared and used to examine the influence of molecular weight distribution on chemically amplified resist performance. This aspect has been studied only for the chain-scissioning resist poly(methyl methacrylate),[18] conventional diazonaphthoquinone–novolac positive resists,[19] and various substituted poly(styrene) negative resists.[20]

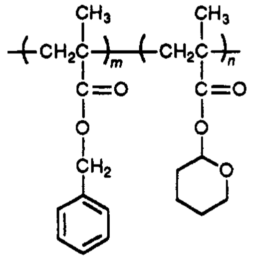
In the following sections we elaborate on some of these concepts and show that high-resolution chemically amplified resists based on the aromatic methacrylate structure can be obtained. We selected the tetrahydropyranyl (THP) group to mask (protect) base-solubilizing groups bound to the polymer and investigated both phenolic and carboxylic acid base-solubilizing groups. We prefer the latter since their inclusion in copolymers with aromatic ballast groups minimizes the volume change that occurs upon acid-catalyzed deprotection. For example, the thickness change upon deprotection of poly(4-tetrahydropyranyloxybenzyl methacrylate), 1, is 33%, a rather high, but somewhat lower value than that for poly(*tert*-butoxycarbonyloxy)styrene), 2 (43%). However, for the 50:50 mol % copolymer of benzyl methacrylate (BMA) and tetrahydropyranyl methacrylate (THPMA, 3) the thickness change upon deprotection is only 24%. Copolymers analogous to 3 have been reported by Ito et. al.,[14] who initially outlined the copolymer approach to minimizing volume loss. However, the 57/43 mol % cumyl methacrylate α-methylstyrene copolymer they described still exhibited a large 38% volume loss upon deprotection. Such changes can be very important during subsequent substrate plasma etching steps where a thick, etch-resistant polymer film is needed. The extensive resist shrinkage that occurs with materials such as 1 and 2 can cause critical dimension changes during plasma etching.



1



2



3

The higher acidity (lower pK_a) of the carboxylic acid moiety is responsible for the very high solubility of 50 mol % methacrylic acid (MAA) copolymers, such as that derived from 3, in aqueous base when compared to phenolic methacrylate homopolymers having 100 mol % phenolic groups. For example, we measured a 100-fold higher dissolution rate for poly(benzyl methyacrylate-*co*-methacrylic acid), containing equimolar monomer, than for poly(4-hydroxybenzyl methacrylate). In this study we discuss only those results obtained for the methacrylic acid copolymers since they exhibit the best overall properties.

---

(13) Schwalm, R. J. *Electrochem. Soc.* **1989**, *136*, 3471.

(14) (a) Ito, H.; Ueda, M. *Macromolecules* **1988**, *21*, 1475. (b) Ito, H.; Ueda, M.; Ebina, M. In Polymers in Microlithography; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; ACS Symp. Series 412; American Chemical Society: Washington D.C., 1989; pp 57–73.

(15) Egitto, F. D.; Vukanovic, V.; Taylor, G. N. In *Plasma Deposition, Treatment and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: New York, 1990; Chapter 5, pp 321–422.

(16) Sandler, S. R.; Karo, W. *Polymer Syntheses*; Academic Press: New York, 1974; Vol. 1 Chapter 10, pp 266–308.

(17) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, P. V. *J. Am. Chem. Soc.* **1983**, *105*, 5076.

(18) Deckman, H. W.; Dunsmuir, J. H. *J. Vac. Sci. Technol., B1* **1983**, 1166.

(19) Hanabata, M.; Uetani, Y.; Furuta, A. *Proc. SPIE* **1988**, *920*, 349.

(20) Feit, E. D.; Stillwagon, L. E. *Polym. Eng. Sci.* **1980**, *20*, 1058.

Experimental Section

(A) Materials. Benzyl methacrylate (Polysciences, Inc.) was used as received for radical copolymerization with methacrylic acid. It was passed over a column of basic alumina under an argon atmosphere prior to use in group-transfer polymerization. Methacrylic acid (Aldrich Chemical Co.) was distilled prior to use in polymerization and used as received for reaction with dihydropyran. 3,4-Dihydro-2*H*-pyran (Aldrich) was distilled prior to use. General procedures for carrying out group-transfer polymerization and the preparation of 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene were described earlier.[21a] Tetrabutylammonium biacetate was prepared by the general procedure of Dicker and co-workers.[21b] Tetramethylammonium hydroxide (TMAH) from Fluka and tetrabutylammonium hydroxide (TBAH) from Fluka were obtained in aqueous solution (2.25 M), and morpholine (Aldrich) was used as received. Low-sodium MOS grade reagents (Fisher) were used to make up coating solutions (cyclopentanone, 1,2-dimethoxyethane, anisole, etc.).

Poly(benzyl methacrylate-*co*-methacrylic acid). To a 2-L, three-necked flask fitted with an Ar gas inlet, a mechanical stirrer, a thermometer, and a condenser was added a solution comprised of 57.8 g (0.35 mol) of BMA in 940 mL of methyl ethyl ketone (MEK) by passing it through a basic alumina filter cake. To this was added 13.36 g (0.15 mol) of MAA and the mixture was cooled to 5 °C. The solution was purged with Ar for 30 min and brought to reflux, and 2.0 g of benzoyl peroxide in 10 mL of MEK was added to initiate polymerization. After refluxing for 4 h the reaction was quenched by the addition of 0.1 g of *p*-methoxyphenol and cooled. The MEK solution was added dropwise to 4 L of hexane to precipitate the copolymer. After reprecipitation from MEK as above, 50.5 g (71%) of BMA–MAA copolymer was obtained after drying under vacuum at 40 °C for 24 h. The copolymer composition in the polymer were obtained by ^{1}H NMR analysis for the aromatic protons at 7.4 ppm and the methyl protons from 0.4 to 1.1 ppm. This preparation afforded a polymer containing 68 mol % of BMA and 32 mol % of MAA. Molecular weight was determined by gel permeation chromatography and is given in units of polystyrene equivalent molecular weight; typical values ranged from 20 000 to 30 000 g/mol. Copolymers of different compositions were obtained by varying the monomer concentrations. Poly(benzyl methacrylate) was prepared using an identical method.

2-Tetrahydropyranyl Methacrylate. This synthesis was based on those of Kearns et al.[27] and Armstrong.[28] To a 1-L, four-necked flask fitted with a reflux condenser, addition funnel, thermocouple well, and a nitrogen gas inlet were added 125 mL of 3,4-dihydro-2*H*-pyran and 15 drops of 50% sulfuric acid. From the dropping funnel was added a mixture of 116 mL of MAA, 125 mL of 3,4-dihydro-2*H*-pyran, and 1 g of phenothiazine. The temperature of the reaction mixture rose to 80 °C and was maintained at 50 °C for 25 h. After cooling to room temperature, 10 g of solid sodium bicarbonate and 40 g of anhydrous sodium sulfate were added. After stirring for 3 h, the mixture was filtered. The filtrate was treated with 0.5 g of calcium hydride, and the excess dihydropyran was removed at reduced pressure with a rotary evaporator. After addition of another 0.5 g of calcium hydride, 1 g of phenothiazine, and 0.2 g of 2,2-diphenyl-1-picrylhydrazyl, double distillation gave 158 g (63%) of 2-tetrahydropyranyl methacrylate (THPMA), bp 67 °C (0.35 Torr). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm, *J* in Hz): 1.56–1.9 (m, 6 H, CH_2), 1.97 (m, $J = 1$, 3 H, CH_3), 3.71 and 3.93 (m, 2 H, CH_2O), 5.62 (m, 1 H, =CH), 6.05 (dd, $J = 3.0$ and 2.75, 1 H, OCHO) and 6.18 (m, 1 H, =CH).

Poly(tetrahydropyranyl methacrylate-*co*-benzyl methacrylate) by Group-Transfer Polymerization. To a solution of 0.74 mL (2.5 mmol) of 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene and 50 μL of tetrabutylammonium biacetate hexahydrate (0.04 M in tetrahydrofuran, THF) in 75 mL of THF under Ar was added a mixture of 25 mL (25.43 g, 0.1445 mol) of BMA and 24 mL (24.57 g, 0.1445 mol) of THPMA at a rate such that the temperature did not exceed 38 °C. Both monomers had been individually passed through columns of basic alumina under an argon atmosphere just prior to use. NMR analysis of an aliquot of the reaction mixture showed no residual monomer. The product was precipitated in methanol and dried at room temperature to give 47.6 g (95%) of poly(tetrahydropyranyl methacrylate-*co*-benzyl methacrylate). GPC: $\bar{M}_n = 19\,200$, $\bar{M}_w = 21\,000$, $\bar{M}_w/\bar{M}_n = 1.1$. NMR analysis of the copolymer showed the composition to be 1:1 on a molar basis.

Poly(tetrahydropyranyl methacrylate-*co*-benzyl methacrylate) by Radical Polymerization. To a solution of 12 mL of THPMA and 12.5 mL of BMA (both monomers purified separately by passage through basic alumina columns) in 75 mL of ethyl acetate (degassed with nitrogen) under Ar at 75 °C was added 0.15 g of azobisisobutyronitrile. After a total reaction time of 11.5 h and a total catalyst addition of 0.3 g, precipitation in hexane gave 22.2 g of poly(tetrahydropyranyl methacrylate-*co*-benzyl methacrylate). NMR analysis of an aliquot of the reaction mixture showed 92% conversion. GPC: $\bar{M}_n = 22\,000$, $\bar{M}_w = 50\,900$, $\bar{M}_w/\bar{M}_n = 2.3$. The copolymer composition was 1:1 on a molar basis as determined by NMR.

Methyl 4-(Tetrahydropyranyloxy)benzoate. This preparation was derived from two previous methods.[29,30] To a stirred mixture of 157 mL (1.72 mol) of 3,4-dihydro-2*H*-pyran, 300 mL of dichloromethane, and 131 g (0.86 mol) of methyl 4-hydroxybenzoate was added 5 drops of 20% sulfuric acid. Addition of the acid caused the ester to dissolve and the temperature to rise 6 °C. After stirring for 20 h, the solution was evaporated, and the residue was dissolved in ether and passed through a short column of basic alumina. The eluent was evaporated to small volume, and 144.7 g (80%) of methyl 4-(tetrahydropyranyloxy)benzoate crystallized as an off-white solid, mp 70 °C. ^{1}H NMR ($CDCl_3$) 1.5–2.1 (m's, 6 H, CH_3), 3.87 (s, 3 H, OCH_3), 5.49 (t, $J = 3.6$, 1 H, OCHO), 7.06 (d, $J = 9$, 2 H, ArH), 7.97 (d, $J = 9$, 2 H, ArH). IR (CCl_4) 1722 cm^{-1} (ester C=O).

4-(Tetrahydropyranyloxy)benzyl Alcohol. To a mechanically stirred slurry of 10 g of lithium aluminum hydride and 100 mL of THF was added dropwise with cooling in an ice bath a solution of 32.9 g (0.14 mol) of methyl 4-(tetrahydropyranyloxy)benzoate at a rate such that the temperature did not exceed 30 °C. After stirring 18 h at room temperature, the solution was treated cautiously with 100 mL of water. The mixture was filtered, and the filtrate was stirred with 200 mL of aqueous sodium hydroxide for 2 h. The organic layer was separated and evaporated with a rotary evaporator. The residue was dissolved in 200 mL of ether, washed three times with 5% aqueous sodium bicarbonate and dried over sodium sulfate. Evaporation gave 20.6 g (71%) of 4-(tetrahydropyranyloxy)benzyl alcohol as an oil that was not purified further. ^{1}H NMR (THF-d_8) 1.45–2.0 (m's, 6 H, CH_2), 3.50 (m, 1 H, OCH_2), 3.80 (m, 1 H, OCH_2), 4.25 (t, $J = 6$, 1 H, OH), 4.45 (d, $J = 6$, 2 H, $ArCH_2O$), 5.35 (t, $J = 3$, 1 H, OCHO), 6.95 (d, $J = 8$, 2 H, ArH), 7.19 (d, $J = 8$, 2 H, ArH). The IR spectrum showed no ester C=O.

4-(Tetrahydropyranyloxy)benzyl Methacrylate. To a stirred solution of 399 g (1.9 mol) of 4-(tetrahydropyranyloxy)benzyl alcohol, 0.1 g of phenothiazine, and 374 mL of triethylamine in 1140 mL of dichloromethane and 1140 mL of diethyl ether cooled in an ice bath was added dropwise 204 mL (0.33 mol) of redistilled methacrylyl chloride (bp 98 °C) at a rate such that the temperature did not exceed 25 °C. After stirring for 2.0 h at room

---

[21] (a) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (b) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W.; Laganis, E. D.; Sogah, D. Y. *Ibid.* **1990**, *23*, 4034.

[22] *Lange's Handbook of Chemistry*; Dean, J. A., Ed.; McGraw-Hill: New York, 1973; Section 5-8. *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. 69, p D161.

[23] Neenan, T. X.; Houlihan, F. M.; Reichmanis, E.; Kometani, J. M.; Bachman, B. J.; Thompson, L. F. *Proc. SPIE* **1989**, *1086*, 2; *Macromolecules* **1990**, *23*, 145.

[24] Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.* **1976**, *56*, 383.

[25] Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.

[26] Moreau, W.; Merritt, D.; Moyer, W.; Hatzakis, M.; Johnson, D.; Pederson, L. *J. Vac. Sci. Technol.* **1979**, *16*, 1989.

[27] Kearns, J. E.; Mclean, C. D.; Solomon, D. H. *J. Macromol. Sci.—Chem.* **1974**, *A8*, 673.

[28] Armstrong, J. R. Canadian Patent 672,947, 1963.

[29] Kuroda, T.; Hisamura, K.; Matsukuma, I.; Nishikawa, H.; Nakamizo, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 674.

[30] Pinhey, J. T.; Phan, T. X. *Aust. J. Chem.* **1988**, *41*, 69.

temperature the mixture was filtered, the filter cake rinsed with 1 L of ether, and the filtrate evaporated. The residue was dissolved in 1 L of ether and washed with 600 mL of aqueous sodium bicarbonate. The organic layer was dried over sodium sulfate and evaporated under reduced pressure to give an oil. Upon seeding with a few crystals, obtained by cooling a small sample to −78 °C, the oily slowly crystallized. Recrystalization from 1.25 L of hexane at −78 °C gave 280 g of colorless crystals of 4-(tetrahydropyranyloxy)benzyl methacrylate, mp 35.8–36.2 °C, a second crop of 87.5 g (mp 34–35 °C) was obtained from the filtrate (yield 70%). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.96, H, 7.18. ^1H NMR (THF-d_8) 1.5–1.8 (m, 6 H, CH_2), 1.90 (m, 3 H, MeC=C), 3.50 (m, 1 H, OCH_2), 3.80 (m, 1 H, OCH_2), 5.07 (s, 2 H, $ArCH_2O$), 5.40 (t, J = 3, 1 H, OCHO), 5.52 (m, 1 H, =CH), 6.05 (m, 1 H, =CH), 7.0 (m, 2 H, ArH), 7.27 (m, 2 H, ArH). IR (CCl_4) 1720 (conjugate ester C=O) and 1640 cm^{-1} (C=C).

Poly(4-(tetrahydropyranyloxy)benzyl methacrylate). To a solution of 0.64 mL (2 mmol) of 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene, 0.55 mL of tetrabutylammonium biacetate (0.04 M in THF), and 0.06 mL of bis(dimethylamino)methylsilane in 40 mL of THF was added dropwise a solution of 20 g (72.5 mmol) of 4-(tetrahydropyranyloxy)benzyl methacrylate (purified by passing through a column of basic alumina in hexane solution, followed by evaporation of the hexane under reduced pressure in 30 mL of THF. When the exothermic polymerization was finished and the temperature had returned to room temperature, the reaction mixture was poured into methanol. Filtration gave 19 g (95%) of poly-(4-(tetrahydropyranyloxy)benzyl methacrylate). GPC: $\bar{M}_n$ = 9390, $\bar{M}_w$ = 11 500, $\bar{M}_w/\bar{M}_n$ = 1.23. DSC: T_g = 62.3 °C, with a decomposition endotherm at 250.5 °C. TGA: rapid weight loss of 24.74% at 248 °C.

Photoactive Compound Synthesis. The preparations of 2,6-dinitrobenzyl tosylate and mesylate have been described elsewhere.[23] Bis(4-*tert*-butylphenyl)iodonium chloride was prepared by the method of Crivello.[24] The syntheses of various diphenyliodonium and triphenylsulfonium salts were adapted from the literature.[24,25]

1,3-Benzenedisulfonate Bis Silver Salt. A 50-mL round-bottomed flask was charged with 20 mL of distilled water and 5.00 g of 1,3-benzenedisulfonyl chloride. The resulting suspension was stirred under reflux for 4 h, at which time a clear solution was obtained. The mixture was heated under vacuum to remove most of the water and all of the hydrochloric acid. Then crude acid was redissolved in 50 mL of distilled water, and 5.30 g of silver carbonate was added slowly. Effervescence ceased during the addition of the last few portions. The aqueous solution was filtered to remove any excess silver carbonate. The solution was stripped of water under vacuum and the resulting white crystalline solid was crushed and dried under high vacuum overnight in the presence of P_2O_5. In this way 8.1 g (93%) of silver salt was obtained. Anal. Calcd for $C_6H_4Ag_2O_6S_2$: C, 15.95; H, 0.89; S, 14.19. Found: C, 15.66; H, 1.17; S, 14.83. ^1H NMR (DMSO-d_6) 7.32 (t, J = 7.5, 1 H), 7.57 (d, J = 7.5, 2 H), 7.98 (s, 1 H, aromatic protons). IR (KBr) 1400 (w, aromatic C=C), 1175 (vs, S=O), 1090 (m, C–S), and 1015 (m, S–O).

Bis(bis(4-*tert*-butylphenyl)iodonium) 1,3-Benzenesulfonate. A solution was prepared consisting of 1.90 g (4.42 mmol) of bis(4-*tert*-butylphenyl)iodonium chloride dissolved in 100 mL of dichloromethane. To this solution was added with stirring 1.00 g (2.21 mmol) of the bis silver salt of 1,3-benzenedisulfonic acid dissolved in 25 mL of water. Upon addition of the silver salt the precipitation of silver chloride occurred, and the reaction mixture was left stirring overnight at room temperature. Then it was filtered and separated into aqueous and organic layers. The organic layer was extracted several times with 25-mL aliquots of water, dried over anhydrous magnesium sulfate, filtered, and stripped of solvent to give 2.13 g (94%) of a tan solid. Anal. Calcd for $C_{46}H_{56}I_2O_6S_2$: C, 54.01; H, 5.52; S, 6.27. Found: C, 53.56; H, 5.64; S, 6.16. ^1H NMR ($CDCl_3$) 1.21 (s, 36 H, Me), 6.87 (t, J = 7.9, 1 H, ArH), 7.23 (d, J = 8.9, 8 H, I^+ArH), 7.39 (d, J = 7.9, 2 H, ArH), 7.78 (d, J = 8.9, 8 H, I^+ArH), 8.69 (s, 1 H, ArH). IR (KBr) 2995 (m, C–H), 1480 and 1460 (m, C=C), 1220 (vs, C–C), 1190 cm^{-1} (vs, S=O), and 995 cm^{-1} (m, C–S).

Diphenyliodonium Mesylate. The procedure used was the same as for bis(bis(4-*tert*-butylphenyl)iodonium) 1,3-benzenedisulfonate except that the starting materials were 5.00 g (15.79 mmol) of diphenyliodonium chloride and 3.20 g (15.79 mmol) of silver mesylate. The workup differed in that the salt stayed in the aqueous layer. After removal of water the crude residue was recrystallized several times from hot ethanol to give 2.27 g (38%) of white cystals, mp 140–142 °C. Anal. Calcd for $C_{13}H_{13}IO_3S$: C, 41.48; H, 3.45; I, 33.78; S, 8.51. Found: C, 41.03; H, 3.21; I, 33.38; S, 8.43. ^1H NMR (DMSO-d_6) 2.49 (s, 3 H, CH_3S), 7.68 (t, J = 1.8 Hz, 4 H, ArH), 7.78 (t, J = 1.8 Hz, 2 H, ArH) and 8.43 (d, J = 1.8 Hz, 4 H, ArH). IR (KBr) 1469 (m, C=C), 1196 (vs, C–C), 1078 (vs, S=O), 1059 cm^{-1} (m, C–S).

Diphenyliodonium Tosylate. The procedure used was the same as for bis(bis(4-*tert*-butylphenyl)iodonium) 1,3-benzenedisulfonate except that the starting materials were 5.67 g (17.92 mmol) diphenyliodonium chloride and 5.00 g (17.92 mmol) of silver tosylate. After the usual workup, the crude material was recrystallized from a mixture of dichloromethane and ether to give 6.97 g (9%) of a white solid. Anal. Calcd for $C_{19}H_{17}IO_3S$: C, 50.44; H, 3.76; I, 28.10; S, 7.08. Found: C, 50.40; H, 3.76; I, 28.08; S, 7.53. ^1H NMR ($CDCl_3$) 2.30 (s, 3 H, CH_3Ar), 7.42 (d, J = 7.2, 2 H, ArH), 7.20–7.70 (m, 8 H, ArH), 8.04 (d, J = 7.2, 4 H). IR (KBr) 1471 (m, C=C), 1196 (vs, C–C), 1186 (m, S=O), and 1041 cm^{-1} (m, C–S).

(B) Analytical Measurements and Lithographic Processing. Exposures were conducted using either a Süss Model MA56 deep-UV contact printer or a GCA Model 4200 Laserstep exposure tool. Both machines had KrF excimer laser light sources emitting at 248 nm. Nicolet DX5 and 360WB Fourier transform infrared (FTIR) spectrometers were used to obtain IR spectra of films that were spin coated on double-side-polished Si wafers. Ultraviolet (UV) spectra were recorded on quartz substrates using a Perkin-Elmer Model 330 spectrophotometer. NMR spectra were recorded using a Bruker Model 360AM spectrometer and a General Electric Omega 500 spectrometer.

Differential scanning calorimetry (DSC) was conducted with a Perkin-Elmer Model DSC-4 or a Dupont Instruments Model 9900. The instruments were calibrated with an In standard at heating rates of 10 and 20 °C/min. Films were removed from Si wafers by scraping and placed in the DSC pan as fine powders. A hole was punched in the pan and heating was begun. Thermogravimetric analysis was conducted with a Dupont Instruments Model 951 thermogravimetric analyzer.

Plasma etching rates were measured in an Applied Materials 8110 hexode reactor. The conditions for etching Al films were 95 sccm of BCl_3, 20 sccm of Cl_2, and 16 sccm of CHF_3, 16 mTorr total pressure, −230 V bias, and a power density of ~0.1 W/cm^2. Half of each test substrate was covered during etching and the film thickness loss was measured with a Dektak IIA profilometer after etching for 25 min, the time to remove a 1-μm-thick Al layer.

After exposure development was conducted in a thermostated bath of dilute aqueous base. The patterned wafers were examined with a Leitz Ortholux optical microscope and a Hitachi Model 2500 SEM.

Results and Discussion

Resin Properties. Copolymers of BMA and THPMA having 50:50 mol % composition were employed based on an evaluation of BMA–MAA copolymers as low-absorbance, base-soluble resins for deep-UV lithography. Solubility determinations in a variety of aqueous base solutions showed that the dissolution rate depended only weakly on resin molecular weight, base concentration, and temperature of the aqueous base used, but depended very strongly on copolymer composition as shown in Figure 2. Rapid dissolution was observed above 35 mol % MAA, whereas no dissolution occurred at lower MAA concentrations. In comparison analogous phenol threshold concentrations for copolymers of *p*-methoxystyrene and *p*-hydroxystyrene[15] and a poly(4-(*tert*-butoxycarbonyloxy)-styrene sulfone) (CAMP)[12] are 75 and 98 mol %, respectively.

To provide an acceptable solubility margin we worked with 50 mol % copolymers of BMA and THPMA. These copolymers have an absorbance of 0.14/μm at 248 nm

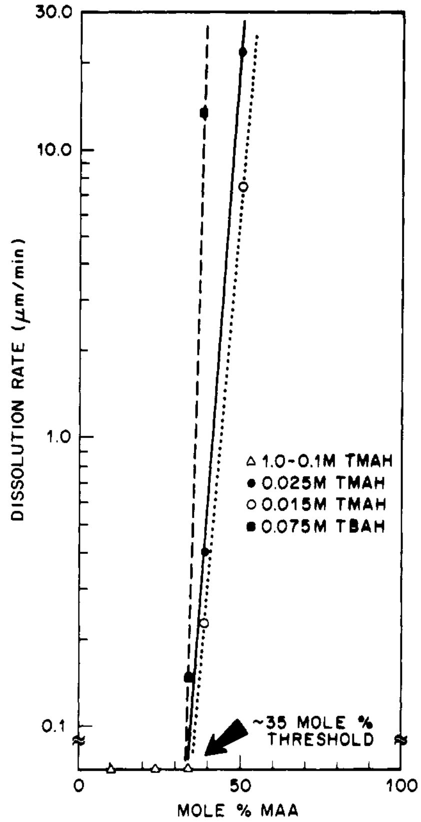


Figure 2. Dissolution rates for 25 000 g/mol BMA-MAA copolymer films as a function of copolymer composition, developer, and developer concentration in aqueous solutions.

Table I. Properties of BMA-THPMA Copolymers

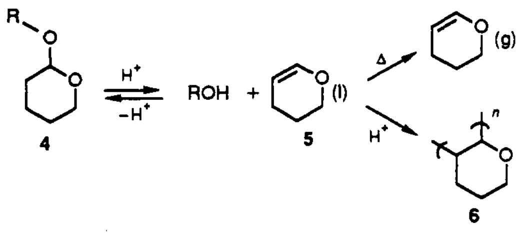
no.	polymerization method	BMA, mol %	$\bar{M}_n$, g/mol	$\bar{M}_w$, g/mol	$P = \bar{M}_w/\bar{M}_n$	T_g, °C
1	GTP	55	16 400	18 000	1.1	94
2	GTP	50	19 000	21 000	1.1	94
3	free radical	50	22 300	51 000	2.3	91

(Figure 3) compared to a value of 0.16/μm for the BMA-MAA copolymer formed upon complete removal of the THP protecting group.

Resins prepared by both group-transfer and free-radical polymerization were used. Their properties are summarized in Table I. All three had similar number average molecular weights averaging about 19 200 g/mol. The ^{13}C NMR spectra were consistent with atactic structures for all three polymers. Samples 2 and 3 were used to study the influence of molecular weight distribution on resist performance.

The T_g values are nearly identical for the three copolymers but are lower than those measured for other chemically amplified resists[6,10] (<110 °C) and poly(methyl methacrylate) (105 °C). (>110 °C) and poly(methyl methacrylate) (105 °C).

Evaluation of Acid Catalysts for Thermal Deprotection. DSC experiments were used to determine the temperature range and rate of thermal deprotection of the THP masking group in the presence of various strong acids. The overall reaction sequence is outlined in eq 1.



(1)

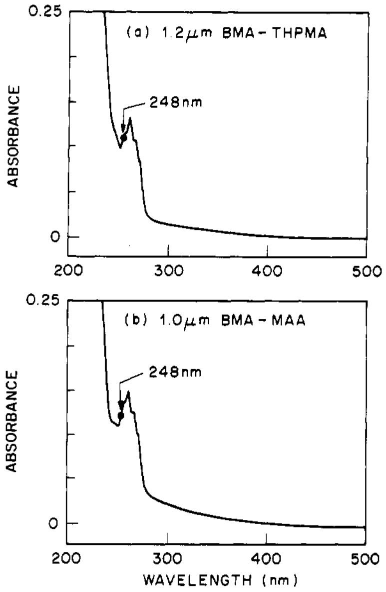


Figure 3. Absorption spectra for BMA-THPMA (a) and BMA-MAA (b) formed by removal of the THP group.

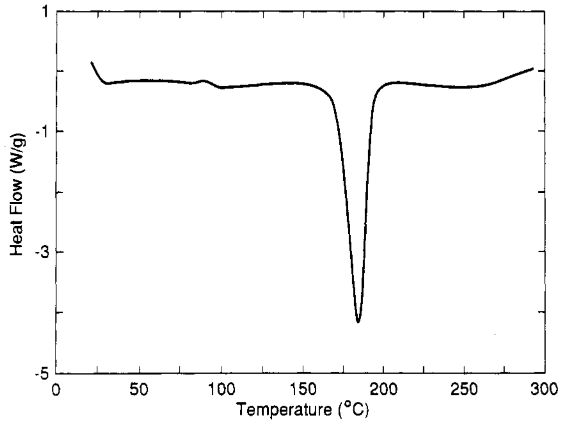


Figure 4. DSC curve at 20 °C/min for BMA-THPMA (5.6 mg).

The initial equilibrium formation of ROH and dihydropyran (**5**, DHP) affords liquid (l) DHP when the reaction is conducted at temperatures <90 °C, its boiling point. In this state acid-catalyzed polymerization to form nonvolatile oligomers **6** or dimers also may occur. Formation of these products in resist films may alter the dissolution (image development) process if they are less soluble in the developer. At temperatures above the DHP boiling point volatile DHP(g) is formed and film loss occurs.

For deep-UV exposure we sought photoacid generators that would absorb 248-nm radiation and efficiently generate strong acids, would deprotect the resist at moderate temperatures, but would not contain inorganic atoms, such as As or Sb, that could form either etch resistant refractory oxides or alter device performance by assimilation into Si device substrate layers.

We examined the reaction catalyzed by two classes of acids dissolved in the BMA-THPMA films, at a concentration of 0.2 mol %, by DSC. Upon heating from room temperature at 20 °C/min, the copolymer without acid catalyst showed a large endotherm having an onset temperature at 170 °C and a temperature at the endotherm maximum at 186 °C (Figure 4). That the observed endotherm corresponds to the thermal decomposition of tetrahydropyranyl carboxylate groups with vaporization of DHP is confirmed by thermal gravimetric analysis (Figure 5) which shows a 24% weight loss between 170 and

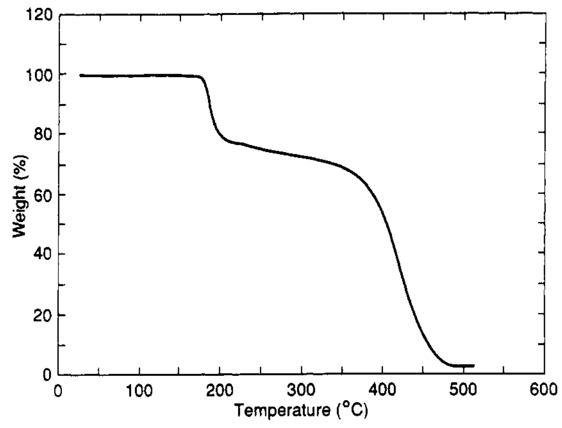


Figure 5. TGA curve at 20 °C/min for BMA–THPMA.

Table II. DSC Results for 1:1 BMA–THPMA Copolymer Mixtures with 0.2 mol % of Various Strong Acids

acid	pK_a[22]	T_{init}, °C	T_{max}, °C
none, control		170	186
maleic	1.8	150	178
oxalic	1.2	120	149
benzenesulfonic	0.7	75	120
1-naphthalenesulfonic	0.6	75	119
2-naphthalenesulfonic	0.6	70	111
p-toluenesulfonic	<0.5	70	116
methanesulfonic		70	113
trifluoromethanesulfonic	<0.1	$\ll$70	

192 °C. This is equivalent to the DHP content in the copolymer. When mixtures of the copolymer and various acids were similarly analyzed by DSC, thermal decomposition occurred at lower temperatures. The temperatures for the endotherm onsets (T_{init}) and maxima (T_{max}) were recorded for various mixtures. These values were reproducible, but the reaction enthalpy, the integral of the endotherm peak, was not. Eight acids from the sulfonic and carboxylic acid classes were tested and gave the results assembled in Table II.

The copolymer itself decomposes very rapidly at temperatures above 170 °C with a maximum rate occurring at 186 °C. Addition of 0.2 mol % of two difunctional carboxylic acids had just a slight catalytic effect at high temperatures. Only oxalic acid showed a moderate tendency to catalyze deprotection. In contrast, all of the sulfonic acids rapidly catalyzed DHP loss and had T_{init} values ranging from 70 to 75 °C and T_{max} values from 111 to 120 °C. The former occurred about 100 °C lower than acid-free samples while the T_{max} values were about 80 °C lower. These results are analogous to those for *tert*-butoxycarbonyl-protected phenolic polymers.[23]

The temperatures needed to deprotect copolymer **3** were somewhat lower when heating was performed on a hot plate at a fixed temperature. In these experiments FTIR spectroscopy of approximately 1-μm-thick copolymer films coated on double-side-polished Si wafers was employed to follow the reactions. Parts a and b of Figure 6 show FTIR spectra of copolymer films heated at 130 and 155 °C for 5 min, respectively. The film heated at 130 °C had a single carbonyl peak near 1730 cm^{-1}, while an additional carbonyl peak at 1680 cm^{-1} was evident in the sample heated at 155 °C. The latter spectrum also showed changes in the hydrogen-bonded OH stretching region near 3000 cm^{-1} and the absence of several peaks in the region 1200–800 cm^{-1}. The spectrum of a 3:2 copolymer of BMA and MAA **7** shown in Figure 6c closely matches that in Figure 6b. These results are in accord with the expected formation of carboxylic acid groups (weaker peak at 1680 cm^{-1}) upon deprotection.

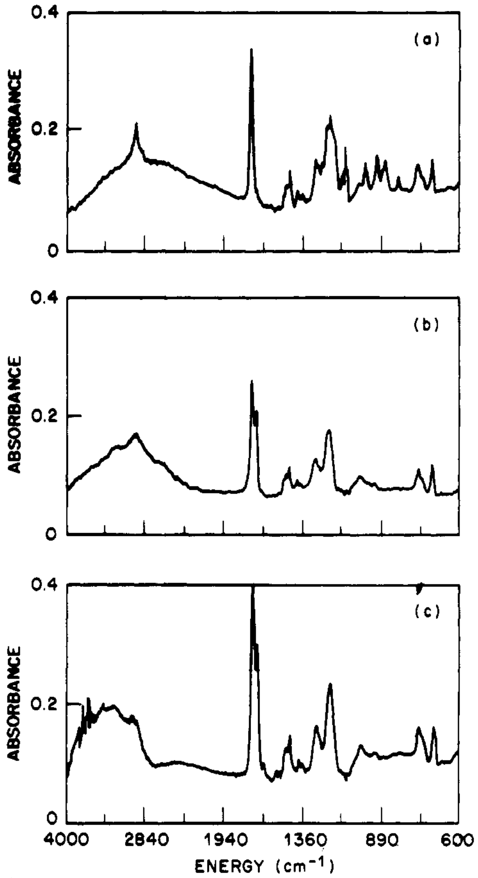
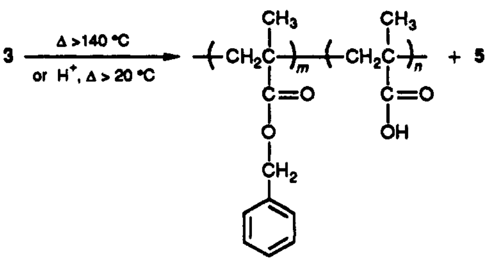


Figure 6. FTIR spectra under N_2 for 1:1 BMA–THPMA films heated at 130 °C for 5 min (a), 155 °C for 5 min (b), and a comparison film of a 3:2 copolymer of BMA and MAA (c).

Other tests also have proved useful in following the deprotection process. The thickness loss upon heating was less than 5% at 130 °C and increased to 23% at 155 °C nearly equal to the weight loss expected (24%) for complete deprotection. The sample heated at 130 °C was insoluble in 0.07 M aqueous TMAH while films heated at 155 °C dissolved at rates exceeding 1 μm/min. These and other results discussed later are consistent with the reaction scheme outlined in eq 2. There is no evidence for any cleavage of the benzylic C–O bond in either reaction mode at temperatures below 180 °C in agreement with previous work.[14]



(2)

7

Lithographic Properties. The lithographic properties of 1:1 copolymer films 1 μm thick were determined for a variety of photoacid generators (PAG), PAG concentrations, and processing conditions. The usual parameters, such as sensitivity and contrast, were measured along with others including resolution, adhesion, thermal stability, etc. Our results are collected in Table III, which lists a variety of sulfonium, iodonium, and covalently bound sulfonate photoacid generators. Their structures are given in Figure

Table III. PAG Effects on the Lithographic Properties of Poly(benzyl methacrylate-*co*-tetrahydropyranyl methacrylate)

no.	PAG	concn, wt %	postbake temp, °C	time, min	sens, mJ/cm^2	γ	resoln, μm	remarks
1	TPST	2.5	25	90.0	40	−2.8	0.6	impractical
2	DPIM	2.0	115	1.0	17	−2	>2.0	
3	DNBM	2.0	85	1.0	16–2	>2.0		
4	DNBT	2.0	115	1.0				unstable
5	DPIT	2.0	115	1.0	5	−2.6	0.8	
	DPIT	0.5	115	1.0	11	−2.8	0.7	
	DPIT	0.5	95	1.0	28	<−10.0	1.0	
6	BDIBDS	2.0	110	1.0	56	−3.0	0.6	

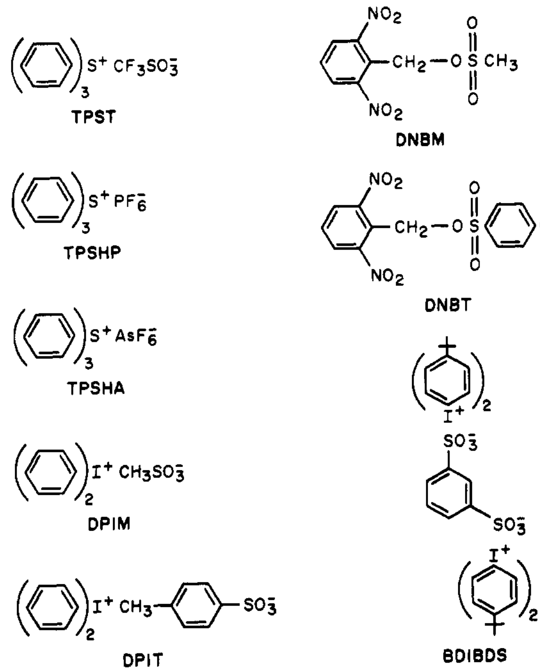


Figure 7. Structures and acronyms for the PAGs employed.

Table IV. Sensitivity and Contrast for Narrow and Broad Molecular Weight Distribution Copolymers Containing 0.5 wt % DPIT

no.	developer	$\bar{M}_w/\bar{M}_n$	development time, min	% overdevelopment[a]	sensitivity, mJ/cm^2	γ
1	0.3 M morpholine	1.1	8	200	14	−2.4
2		1.1	8	200	18	−2.0
3		2.3	8	130	28	−2.2
4		2.3	12	200	12	−2.6
5	0.02 M TMAH	1.1	0.8	200	20	−1.7
6		1.1	1.0	240	10	−3.9
7		2.3	1.0	170	15	−3.0
8		2.3	1.2	200	11	−2.2

[a] The development time divided by the time required to completley dissolve a 1-μm-thick film exposed to 35 mJ/cm^2 of 248-nm light.

7. The developer was aqueous 0.025 M TMAH at 25 °C. Each was prebaked for 1 min at 115 °C prior to exposure.

The triflic acid formed upon irradiation of PAG-1 is such a strong acid that deprotection occurred at room temperature and was complete after about 1.5 h. Resolution was about 0.6 μm, but the processing took too long and exhibited poor reproducibility. All other PAGs required higher temperature processing to initiate deprotection of the THP group. We examined mesylate derivates since they had been reported to be less sensitive.[22] In this case the mesylate derivatives still proved quite sensitive and had good contrast but very poor resolution. We believe that this was caused by rapid diffusion of methanesulfonic acid into the unirradiated regions. Improved resolution was obtained when the postbake temperature and time was reduced, but submicrometer patterns still could not be obtained. Surprisingly, triphenylsulfonium hexafluorophosphate (TPSHP) gave results similar to those of the two mesylates while triphenylsulfonium hexafluoroarsenate TPSHA proved very insensitive and exhibited little thickness loss after postexposure baking.

Two tosylate derivatives also were examined. The dinitrobenzyl ester DNBT proved thermally unstable in the copolymer host. Films containing 2 wt % that were heated for 5 min at 125 °C caused total deprotection as judged by the appearance of the 1680-cm^{-1} peak in the IR region and solubility in dilute aqueous TMAH. Diphenyliodonium tosylate (DPIT) proved more stable but caused some deprotection upon heating at 130 °C for 10 min. Both PAGs appeared to be quite stable as crystalline solids ($T_D \approx 200$ °C by DSC) but were much less stable in solid or liquid solutions. We suspect that this results from the extreme lability of the THP group and the presence of traces of strong acid in the PAGs.

Diphenyliodonium tosylate exhibited the best properties and was more sensitive than the bis(di-*tert*-butylphenyl)iodonium 1,3-benzenedisulfonate (BDIBDS). The latter affords a monoacid upon photolysis that should undergo much slower diffusion than all other acids formed by photolysis of the sensitizers in Table III. For DPIT properties are dependent upon PAG concentration and postbake conditions as shown in Table III. The best resolution was achieved at the lower concentration but is not yet sufficient for very fine line imaging. SEMs of room temperature and higher temperature processed patterns are shown in Figures 8 and 10.

Molecular Weight Distribution Effects. One goal of this investigation was to measure the contrast and sensitivity for formulations having nearly identical number average molecular weight ($\bar{M}_n$) but different molecular weight distributions (P). Sensitivity curves were measured using large area exposures conducted on the deep-UV stepper for 0.5 wt % mixtures of DPIT and the last two coplymers in Table I. Both had $\bar{M}_n$ values close to 20 000 g/mol; however, the polymer prepared by group-transfer polymerization had $P = 1.1$, whereas that prepared by a free-radical method had $P = 2.3$. Films were exposed, baked at 115 °C for 1 min and developed in either 0.025 M TMAH or 0.3 M morpholine aqueous solutions. Figure 9 shows two sensitivity curves in which normalized resist thickness remaining is plotted versus log dose. The intercepts with the x axis (zero thickness remaining) are the sensitivites, while the slopes give the contrast, γ. Using the sensitivity and contrast values obtained from such plots, the performance of the narrow and broader molecular weight distribution copolymers was measured as a function of dissolution conditions including developer type as well as concentration and the degree of overdevelopment. For all experiments multiple determinations were made at constant developer temperature (25 °C). The results are summarized in Table III which also includes

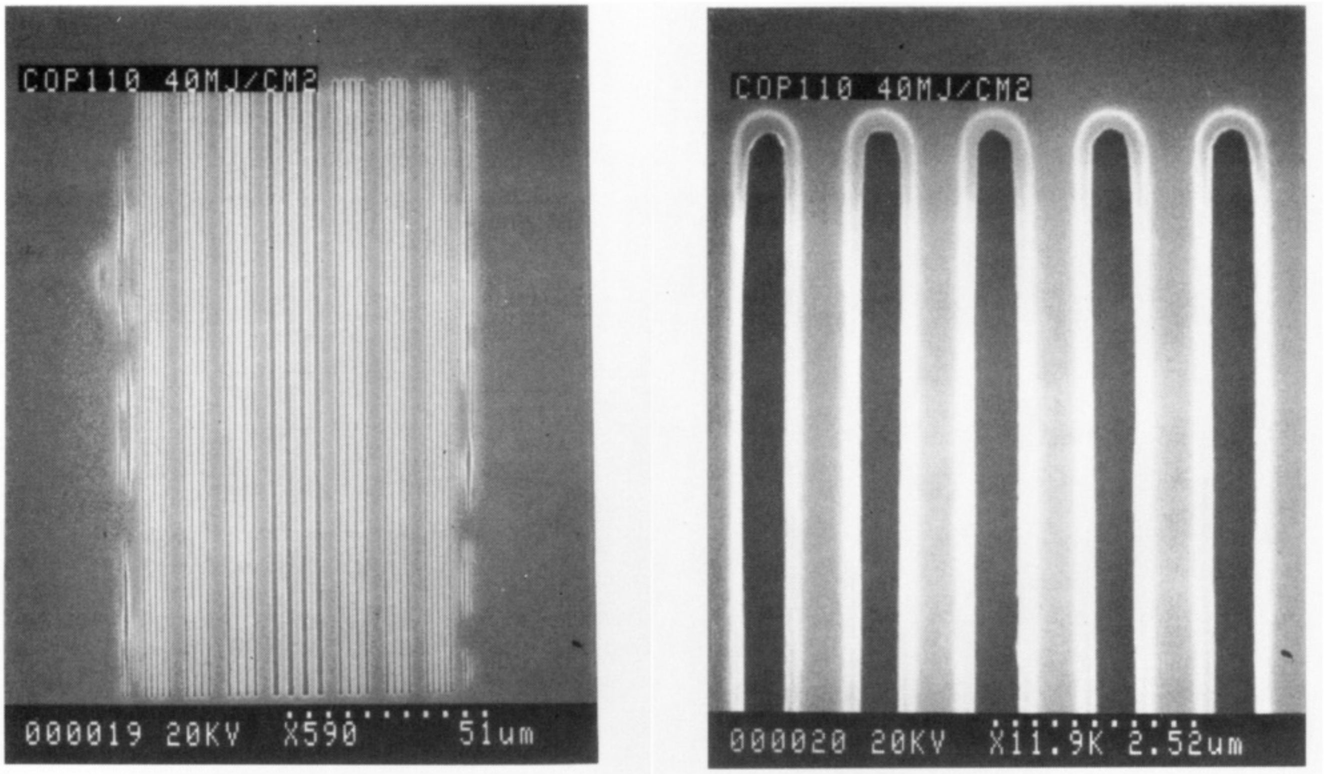


Figure 8. SEM photographs of (a) 2.0, 1.2, 1.0, and 0.8 μm L/s patterns in 0.9-μm thick BMA-THPMA containing triphenylsulfonium triflate and (b) a magnified view of the 0.8 μm L/s.

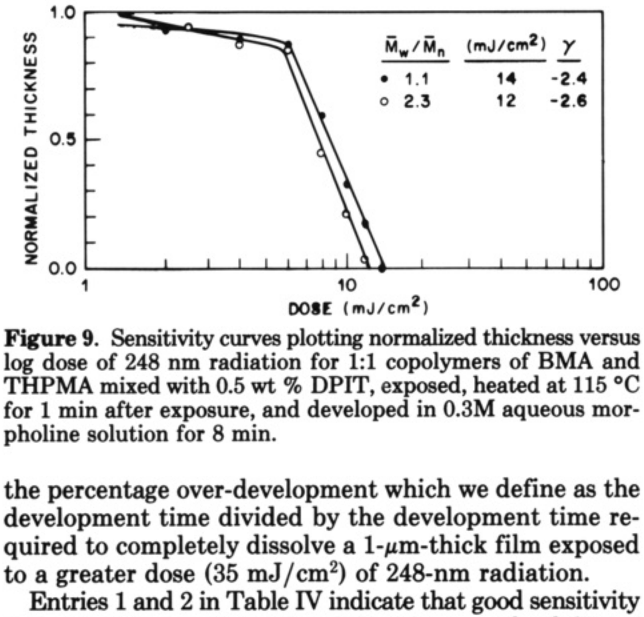


Figure 9. Sensitivity curves plotting normalized thickness versus log dose of 248 nm radiation for 1:1 copolymers of BMA and THPMA mixed with 0.5 wt % DPIT, exposed, heated at 115 °C for 1 min after exposure, and developed in 0.3M aqueous morpholine solution for 8 min.

the percentage over-development which we define as the development time divided by the development time required to completely dissolve a 1-μm-thick film exposed to a greater dose (35 mJ/cm^2) of 248-nm radiation.

Entries 1 and 2 in Table IV indicate that good sensitivity and contrast was achieved and that the reproducibility of these parameters was about ±15%. The two sensitivity curves in Figure 9 show that the linearity in the region of decreasing film thickness is very good all the way from normalized thickness values exceeding 0.9.

Overdevelopment causes sensitivity to increase. For the morpholine developer nearly identical sensitivity and contrast values were obtained for samples 1, 2, and 4 that were overdeveloped to the same degree. A similar comparison for TMAH developer does not give as clear a picture. However, for both developers, the broad molecular weight distribution polymer dissolves at a slightly lower rate. With TMAH and 200% over-development (entries 5 and 8) little dependence on molecular weight distribution was found. Entries 6 and 7 have anomalously high contrast values which may be partially due to the inaccuracies associated with exposing at such low doses, which could only be changed in 2 mJ/cm^2 increments. The overall conclusion from this set of experiments is that molecular weight distribution appears to play no significant role in the behavior of this copolymer resist in this molecular weight range (~20 000 g/mol).

All the results in Table IV were obtained using a 1-min postexposure bake (PEB) at 115 °C. Reduction of the temperature to 95 °C afforded strikingly different results. Overdevelopment (200%) with TMAH solutions gave sensitivies in the range 25–30 mJ/cm^2 and extraordinarily high contrast values (15–25) that were difficult to measure precisely because of the 2 mJ/cm^2 incremental dose limitation on the stepper. Very similar results were obtained for the narrow and broader distribution copolymers and fine features (<1 μm) were not resolved despite the high contrast.

Small strips of exposed resist that received lower doses and were insoluble in the developer often lifted off the substrate during development. Optical microscopic examination of these regions revealed the presence of small holes which increased with increasing dose and eventually merged to form larger holes a doses less than those needed to retain 90% of the initial film thickness. This suggests that liftoff might occur when developer penetrates the resist via such holes and cleaves bonds that normally hold the resist to the substrate.

Such behavior is not observed when the PEB is conducted at 115 °C. One hypothesis possibly accounting for this phenomenon involves the product dihydropyran, which has a boiling point of 90 °C. Residual DHP in the 95 °C heated film is very likely since the processing temperature and DHP boiling point are only 5 °C apart and the substrate is heated dynamically from 25 to 95 °C during the 1-min heating period. Perhaps significant DHP remains in the film heated at lower temperature and forms puddles which are soluble in the aqueous developer leaving holes behind. At 115 °C most of the DHP is volatilized

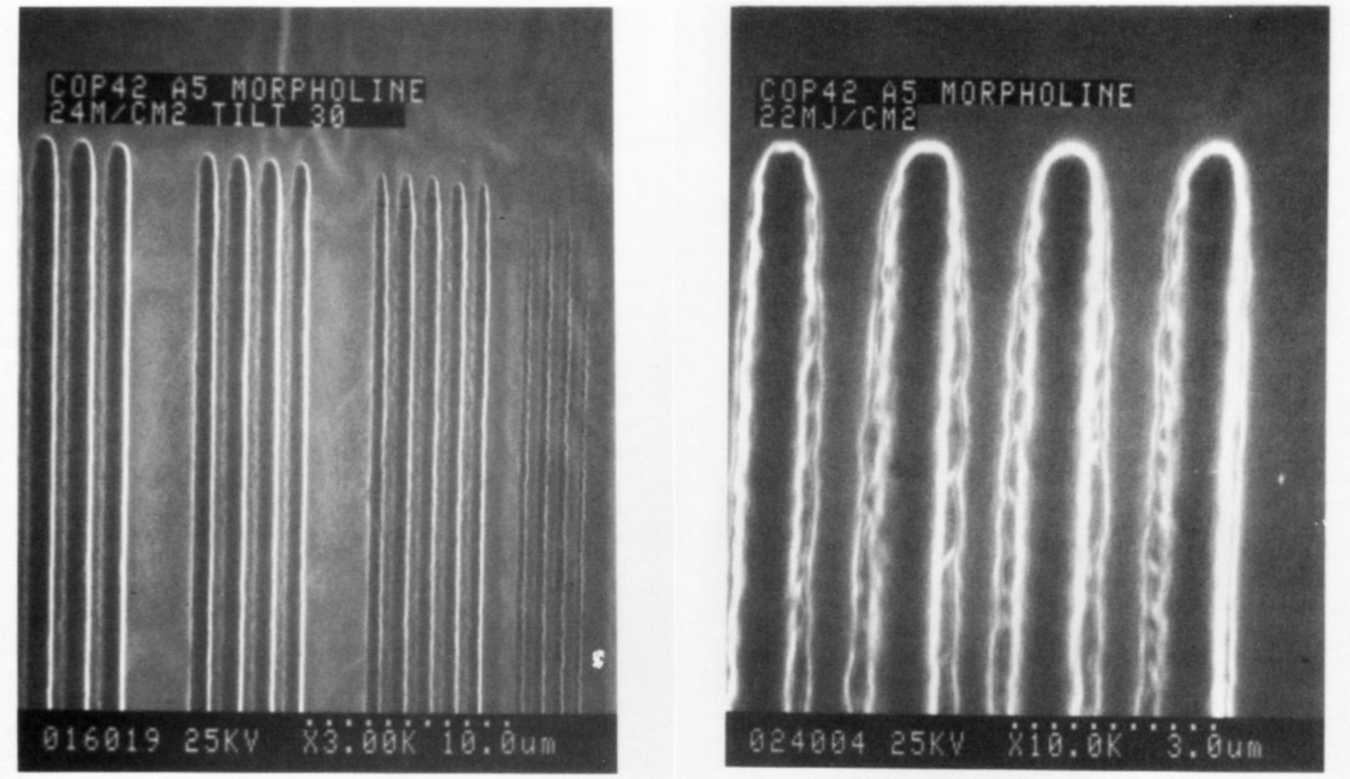


Figure 10. SEM photographs of (a, left) 1.2, 1.0, 0.8, and 0.6 μm L/s features and (b, right) a magnified view of the 0.8-μm lines and spaces in a narrow distribution (P = 1.1) copolymer formulation with 0.5 wt % DPIT. The exposure dose was 24 mJ/cm^2.

Table V. Relative Etching Rate for Various Methacrylate Copolymer Films for Al Plasma Etching as a Function of Processing Conditions

film	processing conditions after spin coating	relative etching rate
HB-HPR-206	200 °C/15 min	1.0[a]
P(BMA)	115 °C/15 min	1.5
P(BMA-*co*-THPMA)	115 °C/5 min	1.7
P(BMA-*co*-THPMA) + 1% DPIT	35 mJ/cm^2 at 248 nm, 115 °C/1 min	1.8
P(BMA-*co*-MAA)	115 °C/5 min	1.8
P(BMA-*co*-MAA)	190 °C/30 min	1.5
P(BMA-*co*-THPMA)	190 °C/30 min	1.6

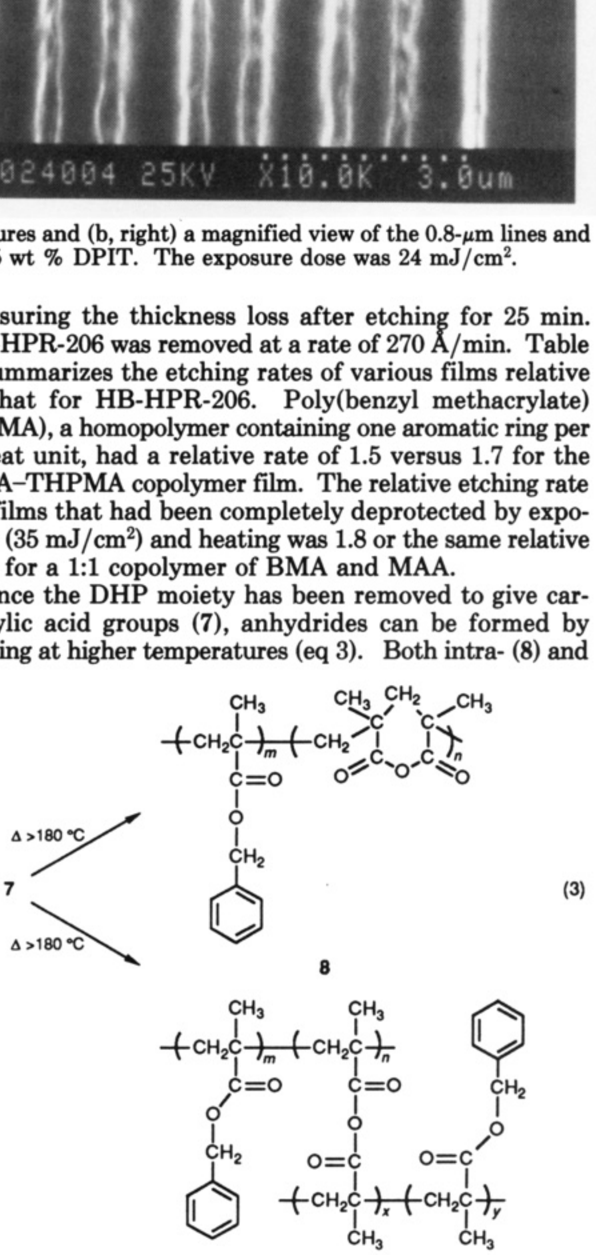
[a] 270 Å/min etching rate for conditions that etch Al at about 450 Å/min.

and thus may not be present at concentrations high enough to form these defects.

Resolution Dependence on Molecular Weight Distribution. The resolution of 1-μm-thick films of narrow and broad molecular weight distribution copolymers containing 0.5 wt % DPIT was determined using optimum exposure, postexposure heating and development conditions. Figure 10 shows an SEM photograph of 1.2, 1.0, 0.8, and 0.6 μm L/s patterns in a narrow molecular weight distribution copolymer film after exposure to 24 mJ/cm^2 of 248-nm light, heating at 115 °C for 1 min and 8 min development in 0.3 M aqueous morpholine. The 0.6-μm patterns were only partially developed and all the features had rough edges as shown by the magnified photograph of the 0.8-μm lines and spaces in the figure. This experiment was repeated several times with each copolymer and the patterns always were the same. Once again resin molecular weight distribution appeared to have no effect on lithographic properties.

Plasma Etching. The etching rates of copolymer and hard-baked (HB) Hunt positive photoresist films (HPR-206) were measured under plasma conditions used to etch aluminum substrates. Etching rates were determined by measuring the thickness loss after etching for 25 min. HB-HPR-206 was removed at a rate of 270 Å/min. Table V summarizes the etching rates of various films relative to that for HB-HPR-206. Poly(benzyl methacrylate) (PBMA), a homopolymer containing one aromatic ring per repeat unit, had a relative rate of 1.5 versus 1.7 for the BMA–THPMA copolymer film. The relative etching rate for films that had been completely deprotected by exposure (35 mJ/cm^2) and heating was 1.8 or the same relative rate for a 1:1 copolymer of BMA and MAA.

Once the DHP moiety has been removed to give carboxylic acid groups (**7**), anhydrides can be formed by heating at higher temperatures (eq 3). Both intra- (**8**) and



intermolecular anhydrides (**9**) can be formed. In at least one previous instance such groups were used to enhance

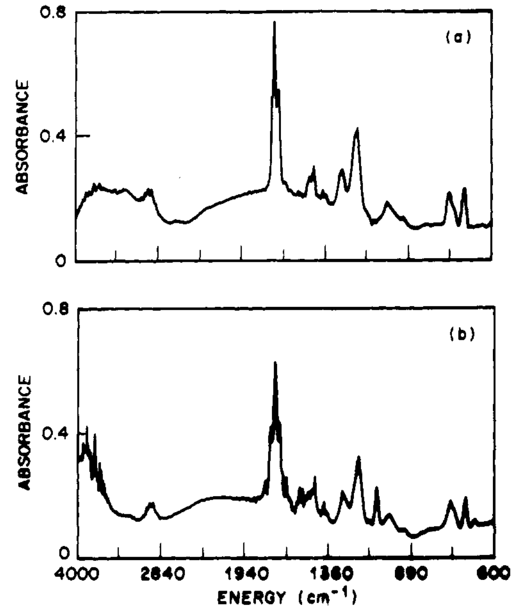


Figure 11. FTIR spectra of BMA–MAA copolymer films heated at (a) 115 °C for 5 min and (b) 190 °C for 30 min.

the etching resistance of methyl methacrylate–methacrylic acid copolymer resists.[26] Heating BMA–MAA at 190 °C for 30 min lowered the relative etching rate from 1.8 to 1.5. The formation of anhydride groups was confirmed by the FTIR spectra (Figure 11) before and after heating. Three peaks appeared in the region between 1600 and 1800 cm^{-1}. The ester carbonyl did not appear to change, but a major peak at about 1770 cm^{-1}, equal in intensity to that of the carboxylic acid group, was evident. This is indicative of anhydride formation as in the new peak at ~1220 cm^{-1} (C–O–C) stretch). The film thickness loss upon heating at 190 °C was 13% and suggests that some benzyl groups also may be lost. The same set of experiments was conducted with a BMA–THPMA copolymer film. In this case the relative etching rate decreased from 1.8 to 1.6, and the spectra were very similar to that in Figure 10b. About 25% film thickness was lost during this step, slightly more than the film thickness loss upon acid catalyzed deprotection at 115 °C (24%). With appropriate processing relative etching rates of ~1.5 can be achieved with the BMA–THPMA copolymer. This value is probably still too high for the etching of Al but is more than adequate for poly-Si, silicide, and oxide etching.

Conclusions

We have prepared and analyzed copolymers of benzyl methacrylate and tetrahydropyranyl methacrylate and evaluated them as sensitive deep-UV resists (<30 mJ/cm^2) when formulated with small amounts (≤2 wt %) of covalent sulfonate esters and onium salt that yield sulfonic acids upon irradiation. Lithographic performance is highly dependent upon the conditions used to thermally deprotect the copolymer and the structure of the photoacid generator. Triflate esters afford acid that is too reactive and initiates deprotection at room temperature, while the less active methanesulfonic acids from mesylate precursors diffuse over large distances (many micrometers) at the temperatures needed for rapid deprotection (115 °C) and prevent submicrometer resolution. Tosylate onium salts exhibit the best overall photocatalytic properties with this copolymer class but slowly initiate deprotection upon standing for more than 2 weeks in solutions used for spin coating. Films of the materials, however, appear quite stable.

With triflate onium salts 0.8-μm lines and spaces are resolved in 1-μm-thick films. Results with diphenyliodonium tosylate are similar except that some edge roughness is apparent on the fine features. Patterns having features ≤0.6 μm in width presently cannot be resolved because of adhesion failure that induces feature liftoff during development.

The contrast values measured using large exposed regions are high (>2) and suggest a potential for even higher resolution. We believe that this has not yet been realized because of diffusion of the acid species over distances equal to those separating the regions we wish to resolve (0.3–0.6 μm). However, larger PAGs such as BDIBDS did not give better resolution and proved less sensitive. Better resolution has not been achieved because of insufficient adhesion. The lithographic properties exhibit no dependence on molecular weight distribution, unlike conventional positive photoresists,[19] because the dissolution rates show only slight changes with molecular weight over a narrow range between 10 000 and 40 000 g/mol. This is true even when both strong (TMAH) and weak (morpholine) aqueous base developers having a 10-fold difference in dissolution rate are used.

The moderate acidity of the carboxyl group appears to be responsible for this behavior, in contrast to that observed for the more weakly acidic phenol group.[6,10,12] In the latter instances no dissolution occurs at low TMAH concentrations. For example, the homopolymer poly(4-(tetrahydropyranyloxy)benzyl methacrylate), which affords poly(4-hydroxybenzyl methacrylate) upon photogeneration of acid and thermolysis, is insoluble in the TMAH developer used for copolymer 3, but is developed when 0.125 M TMAH is used. However, a very high exposure dose is needed (240 mJ/cm^2).

The etching resistance of BMA–THPMA copolymers in a chlorine-based plasma used to etch aluminum is inferior (relative rate = 1.8) to that (1.0) for a hard-baked positive resist film. By thermal processing this value can be improved to 1.5, but an additional 24% of the resist thickness is lost during heating. This loss is less than that for some poly(vinylphenol) based resists (~38%).[6] However, the overall performance does not appear to provide sufficient masking for pattern transfer to aluminum.

These materials are not yet capable of ≤0.5-μm resolution in 1-μm-thick films using deep-UV lithography. Continued materials and process developments may enable attaining this goal. More immediate applications would appear to focus on patterning in much thicker, lower-resolution (>1 μm) films. Future papers will detail the results from these studies.[31]

Acknowledgment. We thank R. Cirelli and M. Cheng for conducting the deep-UV stepper exposures and A. Kornblit and N. Ciampa for testing the polymers under Al plasma etching conditions.

Registry No. 1, 136750-62-4; 3, 119359-85-2; 7, 65697-21-4; TMAH, 75-59-2; DNBT, 114719-51-6; DNBM, 123658-14-0; BDIBDS, 136750-69-1; TPSHP, 57835-99-1; TPSHA, 57900-42-2; morpholine, 110-91-8; 2-tetrahydropyranyl methacrylate, 52858-59-0; 1-(2-(trimethylsiloxy)ethoxy)-1-(trimethylsiloxy)-2-methyl-1-propene, 85248-36-8; tetrabutylammonium diacetate, 51012-12-5; methyl 4-(tetrahydropyranyloxy)benzoate, 106342-09-0; 4-(tetrahydropyranyloxy)benzyl alcohol, 136750-68-0; 4-(tetrahydropyranyloxy)benzyl methacrylate, 136750-61-3; 1,3-benzenedisulfonate bis-silver salt, 136750-63-5; triflic acid, 1493-13-6.

---

(31) Hertler, W. R.; Sogah, D. Y.; Taylor, G. N.; Stillwagon, L. E., to be published.