Chemically Amplified Electron-Beam Photoresists

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Two novel series of electron-beam photoresists possessing high sensitivity and contrast have been developed based on chemical amplification chemistry. The amplification process relies on the electron-beam-induced generation of acids derived from the decomposition of onium salts to catalytically deblock pendant *tert*-butyl ester groups along the backbone of a photoresist polymer or alternatively similar groups present in dissolution inhibitors.

Introduction

Poly(methyl methacrylate) (PMMA) is a classical electron-beam resist that offers the advantages of extremely high resolution, ease of handling, excellent film-forming characteristics, wide processing latitude, and ready availability.[1] However, PMMA is not very sensitive and lacks reactive ion etch resistance.[2] For these reasons, PMMA is not employed for integrated circuit manufacture but is almost exclusively limited to the fabrication of lithographic masks. Similarly, a wide variety of other substituted acrylates and methacrylates have been examined but suffer from the same drawbacks. Although novolac−diazonaphthoquinone photoresists display high resolution and offer excellent dry etch resistance, they are relatively insensitive to electron-beam radiation. Consequently, the exposure times for such photoresists make their use impractical. There is, therefore, a need for new electron-beam resist chemistries which will address the problems of sensitivity and reactive ion etch resistance while at the same time offering good resolution and contrast characteristics.

In recent years, analogous problems associated with UV-sensitive photoresists have been addressed by the development of new classes of deep UV photoresists based on chemical amplification.[3−5] Typically, in a chemical amplification photoresist, a photosensitive acid generator (PAG) is decomposed to produce a strong acid during the exposure. Over the course of the past several years, a considerable variety of PAGs have been developed including diaryliodonium and triarylsulfonium salts[6] and tosylate esters of substituted nitro- and dinitrobenzyl alcohols.[7−9] After release of the acid, a subsequent acid-catalyzed thermal reaction takes place which renders the exposed parts of the photoresist soluble in the case of positive photoresists or insoluble in negative photoresists. One such approach to the design of a new chemically amplified photoresist is shown in Scheme 1.[6]

The high sensitivity of this photoresist system derives from a photomultiplication effect which is produced by the generation of a catalytic amount of acid that results in the deblocking of many *tert*-butoxy groups. Thus, when poly(4-*tert*-butoxy-α-methylstyrene) is subjected to imagewise irradiation in the presence of an onium salt photoinitiator, poly(4-hydroxy-α-methylstyrene) is produced in the irradiated areas after a postexposure bake. This latter polymer can be preferentially removed from the unchanged poly(*tert*-butoxystyrene) by dissolution in aqueous base. Recently, there have been several reports of attempts to develop electron-beam resist systems based on chemical amplification. X-ray and electron-beam resists have been reported which exhibit both high sensitivity and resolution.[10,11] Efforts in this laboratory in the past several years have led to the development of several novel deep-UV photoresists with high sensitivities and contrast.[12,13] It appeared attractive to evaluate these and other related systems as electron-beam resists.

Experimental Section

Materials. Poly(di-*tert*-butyl fumarate-*co*-allyltrimethylsilane) (poly(DtBF-*co*-ATS)), 2.6:1 copolymer, M_n = 12 300 g/mol, M_w = 13 300 g/mol), poly(di-*tert*-butyl fumarate-*co*-styrene) (poly(DtBF-*co*-ST)), 1.38:1 copolymer, M_n = 24 300 g/mol, M_w = 66 700 g/mol) copolymers[12] and poly(4-*tert*-butoxystyrene) (poly(BMST), M_w = 10 900 g/mol) were prepared as described in previous papers.[12,13] Similarly, the preparation of *tert*-butyl cholate was also previously described.[14] Poly(4-hydroxystyrene-*co*-styrene) (8:2 copolymer, M_n = 10 300 g/mol, M_w = 12 000 g/mol) was used as received from the Shin-Etsu Co. The photoinitiator, (4-(*n*-decyloxy)-phenyl)phenyliodonium hexafluoroantimonate was prepared according to established procedures.[13] Metal-free photoresist

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(1) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*; ACS Symp. Ser. 219, American Chemical Society: Washington, DC, 1983; p 122.

(2) Sheats, J. R. *Solid State Technol.* **1989**, *32* (6), 79.

(3) Thompson, L. F.; Willson, C. G. *ACS Symp. Ser.* **1983**, *219*.

(4) (a) Tessier, T. G.; Fréchet, J. M. J.; Willson, C. G. *Materials for Microlithography*; ACS Symp. Ser. 266; American Chemical Society: Washington, DC, 1984; p 151. (b) Willson, C. G.; Ito, H. *J. Electrochem. Soc.* **1986**, *133*, 181.

(5) Houlihan, F. M.; Chin, E.; Nalamasu, O.; Kometani, J. M. *Proc. Polym. Mater. Sci. Eng.* **1992**, *66*, 38.

(6) Crivello, J. V.; Lee, J. L.; Conlon, D. A. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 145.

(7) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Proc. SPIE* **1988**, *620*, 67.

(8) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988**, *21*, 2001.

(9) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. Kometani, J. M.; Bachman, B. J.; Thompson, L. *Macromolecules* **1990**, *23*, 145

(10) Ito, H. *Polym. Prepr.* **1990**, *31*(2), 375.

(11) Novembre, A. E.; Tai, W. W.; Kometani, J. M.; Hanson, J. E.; Nalamasu, O.; Taylor, G. N.; Reichmanis, E.; Thompson, C. F. *Proc. SPIE* **1991**, *1466*, 89.

(12) Crivello, J. V.; Shim, S.-Y., *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 513.

(13) Crivello, J. V.; Shim, S.-Y., *Chem. Mater.* **1994**, *6*, 2167.

(14) O'Brien, M. J.; Crivello, J. V. *Proc. SPIE,* **1988**, *920*, 42.

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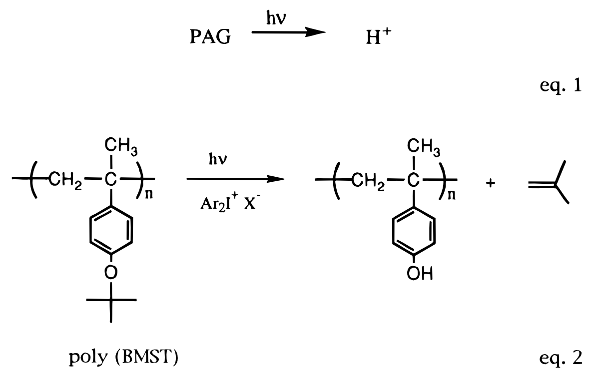
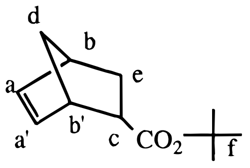
Scheme 1



developer MF-312 tetramethylammonium hydroxide was used as purchased from the Shipley Co.

Measurements. ^{1}H and ^{13}C NMR data were obtained in $CDCl_3$ or benzene-d_6 with a Varian Model XL 200 spectrometer equipped with a Fourier transform accessory. Infrared spectra were taken on a Perkin-Elmer 1800 Fourier transform infrared spectrometer. UV spectra were recorded on a Hitachi U-2000 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained with the aid of a Perkin-Elmer TGA, DSC-7 thermal analysis system at a heating rate of 20 °C/min for TGA and 10 °C/min for DSC in nitrogen. Molecular weights and molecular weight dispersities were measured using a Hewlett Packard 1047A gel permeation chromatograph. The composition ratios of the copolymers were determined by elemental analyses for C, H, and O. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ.

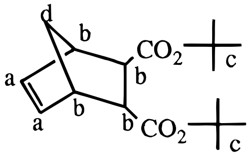
Preparation of *tert*-Butylbicyclo[2.2.1]hept-5-ene-2-carboxylate (IV). Isobutylene (32 mL) was added to a solution of 20 g (0.155 mol) of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid which was dissolved in 80 mL of dichloromethane and cooled to −30 °C. To the resulting mixture 0.5 mL (5.6 mmol) of triflic acid was added and the mixture stirred for 1 h while maintaining the temperature between −20 and −30 °C. Next, 2.5 mL of triethylamine was added and the reaction mixture was warmed to room temperature. The mixture was concentrated under reduced pressure, and the residue was dissolved in ether and washed with 5% HCl, three times with water, and a saturated sodium chloride solution. The residue was dried over anhydrious magnesium sulfate, and concentrated under reduced pressure. There was obtained 17 g (85% yield) of *tert*-butyl bicyclo[2,2,1]hept-5-ene-2-carboxylate after vacuum distillation (bp = 105 °C/ 33 Torr). Elemental Analysis: Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.18; H, 9.40. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.5−6.0 (m, 2H, a,a′), 3.2−2.7 (m, 3H, b,b′,c), 1.7−1.0 (m, 13H, d,e,f).



(IV)

Preparation of Di-*tert*-butylbicyclo[2.2.1]hept-5-ene-2,3-carboxylate. To a 1000 mL, three-neck, round-bottom flask, equipped with a magnetic stirrer, condenser, thermometer, nitrogen inlet, and addition funnel were placed 61.4 g (0.55 mol) of potassium *tert*-butoxide in 600 mL of freshly dried *tert*-butyl alcohol. To this solution was added dropwise 60 g (0.27 mol) of *trans*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid chloride. After about 2−3 mL had been added, an exothermic reaction started and further addition was done at a rate such that the temperature remained about 50 °C. The solution was further heated at reflux for 4 h. At this time, the solution was cooled to room temperature. The solution was poured into water and extracted with ether. The resulting extracts were dried over anhydrious magnesium sulfate and the solvent removed on a rotary evaporator leaving an oil. The pure product was obtained in 72% yield (mp = 38−40 °C) after column chromatography on silica gel using a 3:1 mixture of cyclohexane and ethyl acetate.

Elemental Analysis: Calcd for $C_{17}H_{26}O_4$: C, 69.39; H, 8.84. Found: C, 69.63; H, 8.88. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.5−6.0 (d, 2H, a), 3.5−2.5 (m, 4H, b), 1.5 (d, 18H, c), 1.7−1.0 (m, 2H, d).



Polymerization of Poly(*tert*-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate) [poly(BNC)]. *tert*-Butylbicyclo[2.2.1]-hept-5-ene-2-carboxylate (2.0 g) and 2 mL of di-*tert*-butyl peroxide (DTBP) were placed in a 10 mL one-neck, round-bottom flask and sealed with a rubber serum cap. The tube was flushed with nitrogen and followed by degasing by repeated freeze−thaw cycles under vacuum. After polymerization for 3 h at 150 °C in an oil bath, the resulting solid was dissolved in dichloromethane and precipitated into 50 mL of methanol. There was obtained 1.1 g (55% yield) of poly(BHC) having a M_w = 19 800 g/mol and a M_w/M_n = 2.5.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 3.0−2.0 (broad, 3H), 2.0−1.0 (s, broad, 15H).

Polymerization of Poly(di-*tert*-butyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) [poly(DBNC)]. Di-*tert*-butylbicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylate (2.0 g) and 1.5 mL of di-*tert*-butyl peroxide (DTBP) were placed in a 10 mL one-neck round-bottom flask and sealed with a rubber serum cap. The tube was flushed with nitrogen and degassed several times by repeated freeze−thaw cycles under vacuum. After polymerization for 1 h at 150 °C in an oil bath, the resulting solid was dissolved in dichloromethane and precipitated into 50 mL of methanol at −78 °C. The polymer was recovered by filtration, the filtrate evaporated to 10 mL, and the resulting solid also recovered. By combining the two solid polymers, there was obtained 0.9 g (44% yield) of poly(DBHC) having a M_w = 3200 g/mol and a dispersity (M_w/M_n) = 1.5.

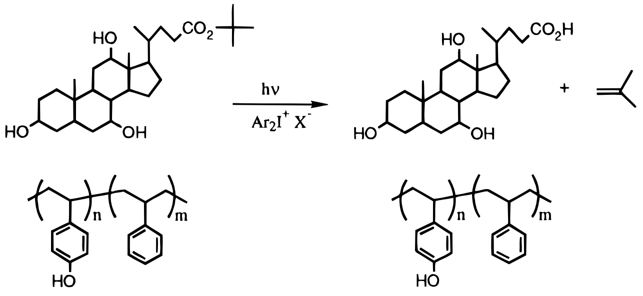
^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 3.0−2.0 (broad, 4H), 1.8−1.0 (s, broad, 22H).

Lithographic Evaluation. A general procedure for the formulation of two-component positive resists consisted of combining poly(DtBF-*co*-ATS) or poly(DtBF-*co*-ST) copolymers with 10 wt % (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate. Three-component photoresists were prepared using 20 wt % poly(BNC) (M_w = 19 800 g/mol, M_w/M_n = 2.5) or poly(DBNC) (M_w = 3200 g/mol, M_w/M_n = 1.5) and 80 wt % poly(4-*tert*-butoxy-*a*-methylstyrene) [poly(BMST)] (M_w = 10 900 g/mol, M_w/M_n = 2.1) with (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (10 wt % of total solids). The films were spin coated to give 0.5 μm thick resists onto 5 in. (12.5 cm) diameter silicon wafers. Electron-beam exposures were performed using a Perkin−Elmer Model No. MEBES I electron beam exposure system at 10 keV. The photoresist films were postexposure baked (PEB) on a hot plate at 100 °C for 10 min and developed in an aqueous base developer (MF-321, from Shipley Co.); (0.21 N) for 1 min. The remaining film thickness was measured using a Nanospec/AFT instrument.

Results and Discussion

Photoresist Compositions and Lithographic Evaluation. A novel chemically amplified positive tone deep-UV photoresist based on dissolution inhibition was recently described by O'Brien and Crivello.[14] This three-part photoresist was composed of a 80:20 poly(4-hydroxystyrene-*co*-styrene) copolymer as the base-

Scheme 2

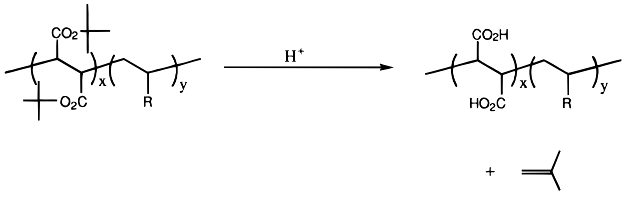


eq. 3

soluble and film-forming polymer. To this copolymer was added 20 wt % of *tert*-butyl cholate as a dissolution inhibitor. Last, this mixture was combined with 0.99 wt % of (4-(*n*-decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate as a PAG. This particular iodonium salt containing a long-chain decyloxy group was purposely chosen because of its excellent photosensitivity and miscibility with the polymer and dissolution inhibitor. The chemistry of image formation by this photoresist is depicted in Scheme 2. Catalytic deblocking of the ester group of *tert*-butyl cholate with the liberation of cholic acid renders the photoresist film soluble where irradiated, thus producing a positive tone image. This photoresist displays a high sensitivity (4 mJ/cm^2) and good contrast ($\gamma = 1.6$). In addition, the photoresist displays excellent oxygen reactive ion etch resistance (~660 Å/min). It, therefore, appeared attractive to evaluate this photoresist as an electron-beam resist. Accordingly, approximately 1.0 μm spin-coated films of the photoresist were subjected to imagewise exposure using a Perkin-Elmer Model No. MEBES I 10 keV electron beam exposure system. The results were very disappointing since no image could be obtained even at high electron-beam doses, i.e., slow scanning speeds, and under a variety of postexposure bake and developing conditions using aqueous base. Although at the time, these results were perplexing, the reasons for the above-described failure of this experiment emerged as other chemically amplified photoresists were evaluated and the mechanism of the interaction of electron-beam irradiation with the components of the photoresist was elucidated. A rationale for the behavior of this and the other chemically amplified photoresists under electron-beam irradiation will be presented later in this article.

Accordingly, we turned our attention to two other chemically amplified photoresist systems developed in this laboratory. These deep-UV sensitive photoresists are copolymers of di-*tert*-butylfumarate with either styrene (poly(DtBF-*co*-ST)) or allyl trimethylsilane (poly(DtBF-*co*-ATS)) together with a diarylidonium or triarylsulfonium salt as a photoacid generator.[12,13] Shown in Scheme 3 are the structures of the two copolymers and the acid-catalyzed deblocking reaction used in image formation. Upon UV irradiation, the onium salts release a Brønsted acid which attacks the pendant *tert*-butyl ester groups along the polymer backbones. In the region of illumination, the polymer is transformed by the deblocking reaction from aqueous base insoluble to soluble due to the formation of the carboxylic acid groups along the backbone of the chain. The two photoresists have not been subjected to extensive optimization but nevertheless display excellent sensitivity (1−4 mJ/cm^2) and contrast ($\gamma = 4.6-6.7$). In addition, these copolymer photoresists possess high glass transition temperatures (>130 °C) and good oxygen reactive ion etch resistance (930−1130 Å/min). On the basis of the above characteristics, we believe that these photoresists have potential applications as deep-UV photoresists.

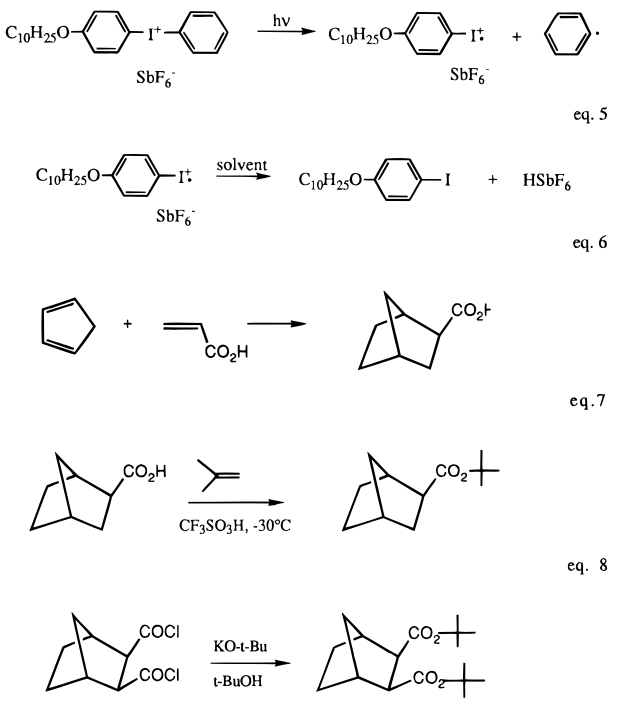
Scheme 3



Where R = C_6H_5 or $CH_2Si(CH_3)_3$

eq. 4

Scheme 4



eq. 5

eq. 6

eq.7

eq. 8

eq. 9

When the latter two photoresists were subjected to imagewise electron-beam irradiation in the presence of 10 wt % (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate, it was observed that both displayed excellent sensitivity and contrast characteristics. Figure 1 and Table 1 show the sensitivity curves and electron-beam characteristics of the two copolymer resists. As shown in Figure 1, the sensitivities of the copolymers/diaryliodonium salt photoresist systems were 2−4 μC/cm^2, and the contrast (γ) was greater than 5. The high sensitivities of these resist systems may be attributed to a chemical amplification effect unique to these photoresist systems. Shown in Figures 2 and 3 are the SEM micrographs of 0.5 μm lines in 0.5 μm thick resists which were exposed and then subjected to a postexposure bake (PEB) of 10 min at at 100 °C. This was followed by development in metal ion-free aqueous base developer for 1 min. The light regions in the photograph represent areas in which the resist has been removed, while the dark regions are due to the unexposed photoresist. While the patterns from poly(DtBF-

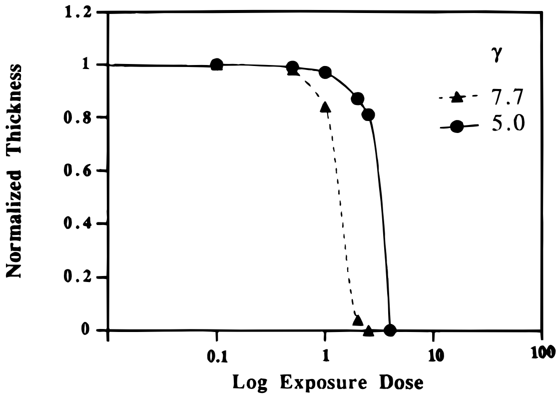


Figure 1. Plots of the normalized thickness versus log dose for the electron-beam exposure of poly(DtBF-*co*-ST) copolymer/onium salt (10/1 wt ratio). (▲) Poly(DtBF-*co*-ATS) copolymer/onium salt (10/1 wt ratio). (●) onium salt = (4-(*n*-decyloxy)-phenyl)phenyliodonium hexafluoroantimonate.

Table 1. Comparsion of the Performance of Several Positive Electron-Beam Photoresists[a]

photoresists	sensitivity (mC/cm^2)	contrast (γ)
poly(DtBF-*co*-ST) copolymer/onium salt (10/1 wt ratio)	2	7.7
poly(DtBF-*co*-ATS) copolymer/onium salt (10/1 wt ratio)	4	5.0
poly(DBNC)/poly(BMST)/onium salt (2/8/1 wt ratio)	10	1.5
poly(BNC)/poly(BMST)/onium salt (2/8/1 wt ratio)	12	1.4

[a] At an accelerating voltage of 10 keV. PEB: 100 °C for 10 min. Development conditions: MF-321 (0.21 N), 1 min.

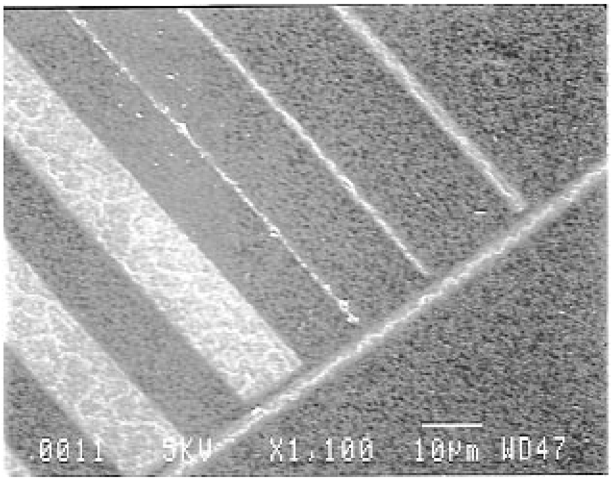


Figure 2. SEM photographs of 2.0, 1.0, 0.5 mm L/S patterns in 0.4 mm thick poly(DtBF-*co*-ATS) copolymer/(4-(*n*-decyloxy)-phenyl)phenyliodonium hexafluoroantimonate (100/5 wt ratio).

co-ATS) (Figure 2) appear well resolved and free of remaining "scum", those from poly(DtBF-*co*-ST) display evidence of traces of residual undissolved photoresist. Further, this latter photoresist appears to give an interesting textured, reticulated appearance which appears to be related to solvent-swelling effects. It should be noted that optimization of the development conditions was not carried out but that it would appear that both of the problems can probably be eliminated or considerably reduced by judicious modification of the developer concentration and the development conditions.

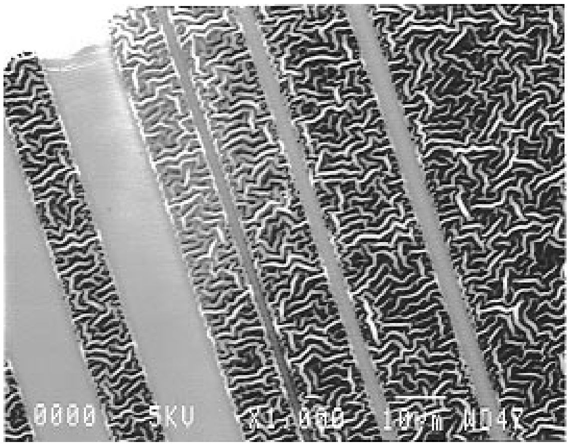


Figure 3. SEM photographs of 2.0, 1.0, 0.5 mm L/S patterns in 0.4 mm thick poly(DtBF-*co*-ST) copolymer/(4-(*n*-decyloxy)-phenyl)phenyliodonium hexafluoroantimonate (100/5 wt ratio).

Attempts to employ a variety of triarylsulfonium salts in place of the diaryliodonium salt photoinitiators in the above electron-beam photoresists produced materials with considerably poorer sensitivities. In contrast, when these same photoinitiators are employed in deep-UV photoresists excellent sensitivities were obtained. It, therefore, appeared that there is a marked difference in the performance of these two basic types of photoinitiators when they are employed for electron-beam photoresist applications.

The excellent results obtained using the above two photoresists contrasts sharply with those of the three component dissolution inhibited chemically amplified photoresist described initially. A consideration of the components present in the two photoresist types revealed that the first photoresist contains phenolic groups whereas the latter two copolymer photoresists do not. This led to the construction of a working hypothesis to account for differences in these two classes of photoresists. The presence of phenolic groups, while essential for the base solubility of the three component photoresist, may impede the electron-beam induced free radical reactions necessary for the generation of acids from the diaryliodonium salt.

To test this hypothesis, two additional novel three component chemically amplified photoresists were prepared. *tert*-Butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate and di-*tert*-butyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate were prepared by the routes shown in eqs 7–9.

Low molecular weight poly(*tert*-butyl bicyclo[2.2.1]-hept-5-ene-2-carboxylate) (poly(BNC), M_w = 19 800 g/mol) and poly(di-*tert*-butyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (poly(DBNC), M_w = 3200 g/mol) were synthesized by free radical polymerization (Scheme 5) as described in the Experimental Section. These polymers undergo efficient deblocking reactions under strong acid conditions but do not possess good oxygen plasma etch resistance. Accordingly, poly(4-*tert*-butoxy-α-methylstyrene)[6] (poly(BMST), M_w = 10 900 g/mol) which possesses good oxygen plasma etch characteristics and, in addition, has deblockable phenolic groups masked by *tert*-butyl groups (eq 12) was used as the major film forming polymer. To 80 wt % of poly(BMST) was added 20 wt % of poly(BNC) or poly(DBNC). It was observed that these polymers were miscibile in each other. The polymer mixtures were sensitized by the addition of 1 wt % of (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluo-

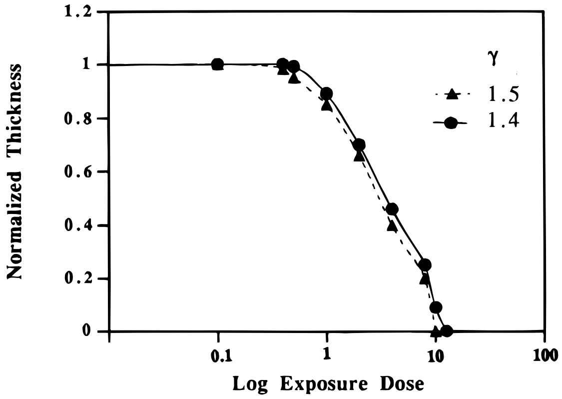
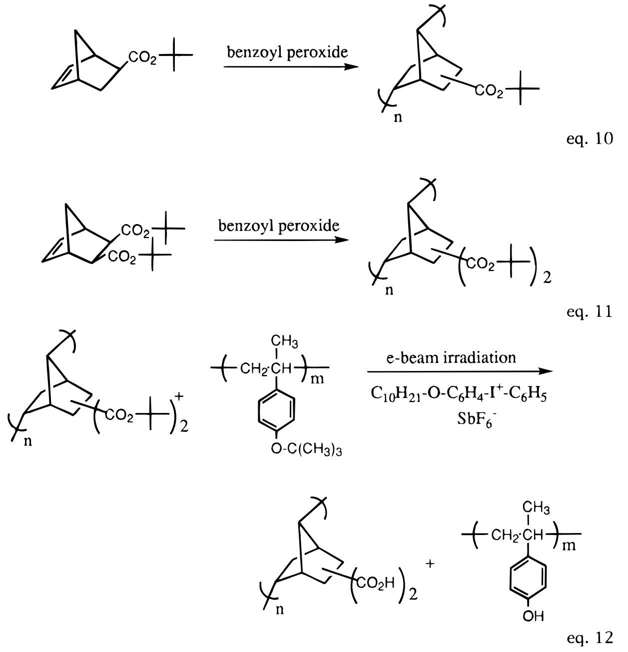


Figure 4. Plots of the normalized thickness versus log dose for the electron-beam exposure of poly(DBNC)/poly(BMST)/onium salt (2/8/1 wt ratio). (▲) Poly(BNC)/poly(BMST)/onium salt (2/8/1 wt ratio). (●) onium salt = (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate.

Scheme 5



roantimonate as a PAG. The electron-beam sensitivity curves for the above two resist systems are given in Figure 4. The sensitivities were 10−12 mC/cm^2, and the contrast was approximately 1.5 (Table 1). Figures 5 and 6 show SEM photographs of 0.5 μm line/space patterns which were produced in these electron-beam resists. Similar effects are noted in these photoresists as previously shown in Figures 2 and 3. A sharper, cleaner image is obtained with poly(4-*tert*-butoxy-α-methylstyrene) dissolution inhibited with poly(BNC) (Figure 6) than with poly(DBNC) (Figure 5). Again, the effects of solvent induced swelling may be noted in Figure 6 which results in a reticulated surface. It is anticipated that this effect can be minimized by optimization of the development conditions.

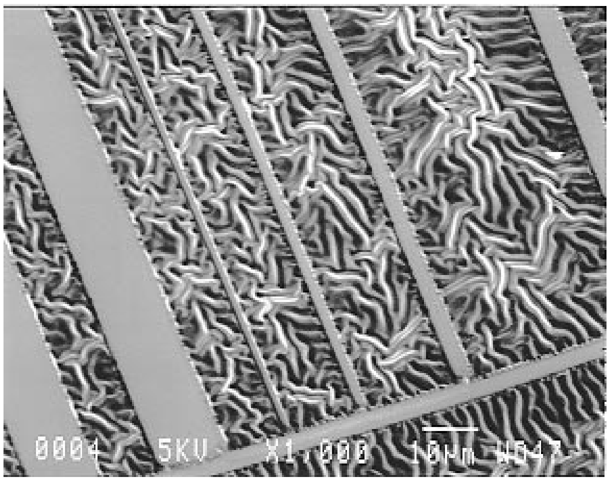


Figure 5. SEM photographs of 2.0, 1.0, 0.5 mm L/S patterns in 0.4 mm thick poly(4-*tert*-butoxy-α-methylstyrene)/poly(DBNC)/(4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (80/20/5 wt ratio).

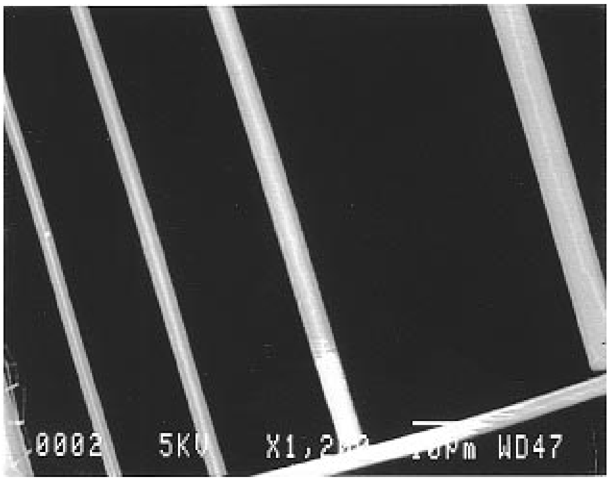


Figure 6. SEM photographs of 2.0, 1.0, 0.5 mm L/S patterns in 0.4 mm thick poly(4-*tert*-butoxy-α-methylstyrene)/poly(BNC)/(4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (80/20/5 wt ratio).

Scheme 6

Pathway 1.

$$M \xrightarrow{e^-} M^{+\cdot} \longrightarrow M^{\cdot} + H^+ \qquad \text{eq. 13}$$

$$M^{\cdot} + Ar_2I^+X^- \longrightarrow ArI^{\cdot} + Ar^{\cdot} + M^+X^- \qquad \text{eq. 14}$$

$$M + Ar^{\cdot} \longrightarrow M^{\cdot} + ArH \qquad \text{eq 15}$$

Pathway 2.

$$Ar_2I^+X^- + e_s^- \longrightarrow ArI^+ + Ar\cdot + X^- \xrightarrow{H^+} HX \qquad \text{eq. 16}$$

Proposed Mechanism of Action. We would like to advance the following mechanism to explain the excellent sensitivity of the photoresist materials described in this investigation and also to explain the reasons for the failure of the first photoresist to respond. The irradiation of all organic materials with electron-beam irradiation generates free radical species by a variety of bond breaking reactions.[15] In addition, secondary or Auger electrons are reemitted by molecules which have absorbed electrons. Both the Auger electrons and the free radicals can interact with diaryliodonium salts. Shown in Scheme 6 is the mechanism which we propose based on studies of the electron-beam-

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[15] Singh, A.; Silverman, J. *Radiation Processing of Polymers*, Hanser Publishers: Munich, 1992; p 1.

induced cationic polymerizations of various vinyl and heterocyclic monomers carried out in this laboratory[16,17] and elsewhere.[18] Electron-beam irradiation of organic compounds and polymers which are designated by **M** in this scheme result in the transient formation of cation-radicals, $\mathbf{M}^{\bullet +}$ (pathway 1). These reactive species relax by bond scission processes to form a variety of radical species and a proton (eq 13). In the second step of this pathway (eq 14), the free radicals interact with the diaryliodonium salt resulting in its irreversible reduction. Simultaneously, $\mathbf{M}^{+}$ cations are formed which react further to generate protons and Brønsted acids. The aryl radicals which are formed in this reaction may further generate $\mathbf{M}^{\bullet}$ radicals as shown in eq 15 by abstraction of a hydrogen. Thus, a catalytic cycle may be set up between eqs 14 and 15 which results in the free radical induced decomposition of the diaryliodonium salt with the production of acidic species capable of promoting the deblocking reaction.

Similarly, by pathway 2, solvated electrons may directly reduce the diaryliodonium salt. A variety of fragments result which give rise to the generation of both protonic acids and cationic species. Diaryliodonium salts are more easily reduced than triarylsulfonium salts[17] and undergo the reactions shown in Scheme 6 most efficiently. Thus, these onium salts are preferred for electron-beam photoresist applications.

The overall result of the reactions shown in Scheme 6 is to generate acidic species capable of inducing the catalytic deblocking of *tert*-butyl ester groups situated on either the backbone of the polymer or in the structure of a dissolution inhibitor. Since the mechanism shown in Scheme 6 depends on the formation of free radicals which in turn lead to the generation of acids, those agents which effectively scavange free radicals should result in marked inhibition or retardation. In a recent publication from this laboratory,[12] the inhibition of the free radical induced decomposion of diaryliodonium salts by typical phenolic free radical scavengers has been reported. The phenolic groups in the 80:20 poly(4-hydroxystyrene-*co*-styrene) copolymer used in photoresist similarly serve as free radical inhibitors and explain why this particular chemically amplified photoresist, while highly sensitive in optical lithography, is insensitive to electron-beam irradiation.

On the other hand, poly(4-*tert*-butoxy-α-methylstyrene) together with poly(BNC) or poly(DBNC) as dissolution inhibitors perform very well as electron-beam photoresists. Although these photoresists rely on the deblocking of poly(4-*tert*-butoxy-α-methylstyrene) to form poly(4-hydroxy-α-methylstyrene) for their ability to be developed in aqueous base, the actual deblocking reaction occurs only after exposure and during the PEB. Thus, phenolic groups are not present during that portion of the reaction scheme when the free radical species are generated by electron-beam irradiation and are required to reduce the onium salt.

The high sensitivity displayed by the electron-beam photoresists based on copolymers poly(DtBF-*co*-ST) and poly(DtBF-*co*-ATS) can also be rationalized in the same way. These photoresists owe their excellent sensitivity to two major factors which include: very facile deblocking of the *tert*-butyl ester groups and the presence of easily abstracted protons in the backbone of those copolymers which enable them to participate in the free radical induced reactions with the photoinitiator.

Conclusions

Four novel electron-beam photoresists have been developed which exhibit high sensitivity and contrast as a result of the chemical amplification induced by onium salt PAGs. The proposed mechanism which explains the action of these photoresists involves the reduction of the onium salt by free radicals and solvated electrons which are generated by electron-beam irradiation bombardment of the photoresist. Reduction of the onium salt results in the formation of an acid which catalytically deblocks *tert*-butyl ester and *tert*-butyl ether groups present either in the backbone of the resist or present in a dissolution inhibitor.

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(16) Crivello, J. V.; Fan, M.; Bi, D. *J. Appl. Polym. Sci.* **1992**, *44*, 9.

(17) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 2143.

(18) Sundell, P-E.; Jönsson, S.; Hult, A. *Polym. Prepr.* **1990**, *31* (2), 373.