Tailoring Transparency of Imageable Fluoropolymers at 157 nm by Incorporation of Hexafluoroisopropyl Alcohol to Photoresist Backbones

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Hexafluoroisopropyl alcohol-functionalized acrylic and styrenic monomers, such as 2-[4-(2-hydroxyhexafluoro isopropyl)cyclohexane]hexafluoroisopropyl acrylate (**2**), 2-[4-(2,2,2-trifluoro-1-methoxy-methoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl acrylate (**3**), and 2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)]styrene (**4**), were synthesized, and their (co)polymers were studied as photoresist platforms for 157 nm lithography. It was found that these (co)polymers are unusually transparent at 157 nm, and absorbances of poly(**2**) and poly(**2**-*co*-**4**) were determined to be 1.93 and 2.38 μm^{-1}, respectively. Results indicated that both electron-withdrawing effects and bulkiness of CF_3 groups play important roles in tailoring the absorbance of chromophores. Lithographic studies were carried out with poly(**2**)-based resists using 157 and 248 nm steppers, and it was demonstrated that, after selective modification, it is possible to use conventional resist backbones, such as acrylic or styrenic polymers, in the design of single-layer resists for 157 nm lithography.

Introduction

The fabrication of increasingly smaller feature sizes for integrated circuits requires advanced lithographic techniques with high resolution.[1−3] Resolution enhancement techniques, using optical proximity correction or phase-shift masks, have demonstrated the fabrication of subwavelength feature sizes at 248 and 193 nm.[3] However, a fundamental solution for enhanced resolution would be to develop lithographic techniques using shorter exposure wavelengths to avoid complexities involved in resolution enhancement techniques. Therefore, with recent improvements in laser technology and optical materials, optical lithography at 157 nm using an F_2 excimer laser light source has emerged as the current choice for post-193-nm technology in the fabrication of devices with feature sizes less than 100 nm.[4]

Protected phenols and carboxylic acids have been utilized as indispensable structural units in the design of conventional 248 and 193 nm resists.[1,5] Deprotection of these protected acidic functions by photochemically generated acid creates large dissolution selectivity between exposed and unexposed areas in an alkaline developer, rendering delineation of mask patterns possible on the silicon wafer surface. Kunz et al. reported that conventional resists containing such acidic functions must be less than 60 nm thick to achieve an optical density of 0.4, which is required to produce a vertical resist wall profile, at 157 nm.[6] Since this is due to the strong absorbance of aromatic and carbonyl groups at this wavelength, the incorporation of transparent acidic functions within a polymer backbone has been an overriding concern in resist design for 157 nm lithography.

It has been reported that fluorine-containing polymers are highly transparent at 157 nm[6] and fluorocarbinols, with pK_a values comparable to those of phenols, can be used as acidic functional groups in the design of chemically amplified and aqueous base developable resists.[7,8] Przybilla et al.[7] introduced hexafluoroisopropyl alcohol (HFIPA) as an alternative acidic group in the design of polystyrene-based resists and dissolution inhibitors for a 248 nm application, and further extension to the 193 nm resist design was made by Ito et al.[8] during the preparation of poly(norbornene sulfone)-based resists. In both cases, HFIPA was incorporated using hexafluo-

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roacetone, and this acidic alcohol was protected by a *tert*-butoxycarbonyl group. Although the poor dry etch resistance of poly(norbornene sulfone)-based resists limits their practical use for lithography,[8] it is notable that when HFIPA-substituted norbornene is used in alternating copolymerization with sulfur dioxide, the resulting copolymer exhibits high transparency at 157 nm with an absorbance of ~3 μm^{-1}.[9] Since this unusual transparency arises from the presence of HFIPA, HFIPA-substituted norbornene monomers have been actively investigated as transparent building blocks in the design of novel resists for 157 nm lithography.[9-12]

In an effort to develop single-layer resists for 157 nm lithography, we have exploited a variety of fluorocarbinol-containing polymers focusing mainly on non-norbornene backbones.[13-16] In the course of screening conventional acrylic and styrenic polymers as potential resist backbones for 157 nm applications, it was found that the transparency of even conventional resist platforms can be significantly enhanced at 157 nm by judicious modification of highly absorbing groups such as aromatic or carbonyl,[16] and similar results were also confirmed by others.[17] In this paper, we report our strategy to develop single-layer resists that are highly transparent at 157 nm using modified acrylic and styrenic backbones.

Experimental Section

Instrumentation. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Inova-400 and Varian VXR-400s spectrometers, respectively. Thermogravimetric analysis (TGA) was performed on a Seiko TG/DTA 220 system at a heating rate of 10 °C/min. Optical spectra of the polymer films were recorded on a VU-301 vacuum UV variable angle spectroscopic ellipsometer (VUV-VASE) instrument (J. A. Woollam Co.) at International SEMATECH. Samples for VUV-VASE measurements were prepared by spin-coating resists on a silicon wafer, primed with hexamethyldisilazane (HMDS) gas, followed by soft-bake at 115 °C for 120 s.

Synthesis of 1,4-Bis(2-hydroxyhexafluoroisopropyl)cyclohexane (1). 1,4-Bis(2-hydroxyhexafluoroisopropyl)benzene (24.6 g, 0.06 mol), dissolved in 70 mL of 2-propanol, was placed in a Parr reactor, and to this was added 3 g of a supported rhodium catalyst (5 wt % on carbon powder).[18] Hydrogenation reactions were typically run overnight under ~600 psi of hydrogen at 130 °C. Upon completion, the heterogeneous solution was filtered to remove the catalyst and the 2-propanol solution was concentrated. The product was purified by fractional distillation at 58−60 °C (0.02 mmHg) to give 23.1 g of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane as a clear oil (93% yield): ^1H NMR($CDCl_3$, 400 MHz): δ 2.85 (s, 1H, $-OH$), 2.22−1.25 (m, 10H, alicyclic C*H* and C*H*$_2$); ^{13}C NMR($CDCl_3$, 100 MHz): δ 123.39 (quartet, $-C(CF_3)_2OH$, $J_{C-F} = 288$ Hz), 78.66 (septet, $-C(CF_3)_2OH$, $J_{C-C-F} = 27$ Hz), 36.25 (alicyclic methine *C*), 23.48 (alicyclic methylene *C*).

Synthesis of 2-[4-(2-Hydroxyhexafluoro-isopropyl)cyclohexane]hexafluoroisopropyl Acrylate (2). To a solution of **1** (30.0 g, 0.07 mol) in 100 mL of dry THF was added 45 mL of 1.6 M *n*-butyllithium (0.07 mol) under nitrogen over a period of 30 min. After 2 h, the resulting solution was treated for 30 min by the dropwise addition of acryloyl chloride (6.5 g, 0.07 mol) dissolved in 100 mL of dry THF. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of 100 mL of distilled water. The aqueous phase was extracted with ethyl ether, and the combined organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography and recrystallization to yield 15.9 g of **2** (49% yield): mp 85−86.4 °C; ^1H NMR($CDCl_3$, 400 MHz): δ 6.48 (dd, 1H, $CHH_{cis}{=}H-$), 6.12 (q, 1H, $CH_2{=}CH-$), 5.98 (dd, 1H, $CHH_{trans}{=}CH-$), 3.20−3.15 (m, methine *H*, adjacent to ester), 3.05 (s, 1H, $-OH$), 2.27−2.21 (m, 1H, methine *H*, adjacent to hydroxyl), 2.05−1.98 (m, 2H, methylene *H* in the ring), 1.93−1.83 (m, 2H, methylene *H* in the ring), 1.70−1.59 (m, 4H, methylene *H* in the ring); ^{13}C NMR($CDCl_3$, 100 MHz): δ 162.11 ($C{=}O$), 133.97 ($CH_2{=}CH-$), 126.95 ($CH_2{=}CH-$), 123.44 (quartet, $-C({=}O)OC(CF_3)_2-$, $J_{C-F} = 288$ Hz), 122.24 (quartet, $-C(CF_3)_2OH$, $J_{C-F} = 288$ Hz), 85.33 (septet, $-C({=}O)OC(CF_3)_2-$, $J_{C-C-F} = 29$ Hz), 79.01 (septet, $-C(CF_3)_2OH$, $J_{C-C-F} = 27$ Hz), 34.64 (methine *C* adjacent to ester), 34.00 (methine *C* adjacent to hydroxyl), 24.01 (methylene *C* adjacent to ester), 21.89 (methylene *C* adjacent to hydroxyl); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ −68.35 ($-C({=}O)OC(CF_3)_2-$), −74.30 ($-C(CF_3)_2OH$).

Synthesis of 2-[4-(2,2,2-Trifluoro-1-methoxy-methoxy-1-trifluoromethylethyl)cyclo-hexane] hexafluoroisopropyl Acrylate (3). To a dispersion of sodium hydride (0.28 g) in dry THF (15 mL) was added 4.7 g of **2** (0.01 mol) dissolved in dry THF (15 mL) at 0 °C. After the mixture was stirred for 1 h at room temperature, chloromethyl methyl ether (0.89 g, 0.011 mol) in 20 mL of dry THF was added dropwise over a period of 30 min at 0 °C. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of distilled water. The aqueous phase was extracted with ethyl ether, and the combined organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography to yield 2.4 g of pure **3** (51% yield): ^1H NMR ($CDCl_3$, 400 MHz): δ 6.48 (dd, 1H, $CHH_{cis}{=}CH-$), 6.12 (q, 1H, $CH_2{=}CH-$), 5.98 (dd, 1H, $CHH_{trans}{=}CH-$), 4.93 (s, 2H, $-OCH_2O-$), 3.44 (s, 3H, $-OCH_3$), 3.23−3.17 (m, methine *H*, adjacent to ester), 2.34−2.29 (m, 1H, methine *H*, adjacent to ether), 2.05−1.99 (m, 2H, methylene *H* in the ring), 1.92−1.86 (m, 2H, methylene *H* in the ring), 1.67−1.56 (m, 4H, methylene *H* in the ring); ^{13}C NMR($CDCl_3$, 100 MHz): δ 161.89 ($C{=}O$), 133.87 ($CH_2{=}CH-$), 127.01 ($CH_2{=}CH-$), 123.27 (quartet, $-C({=}O)OC(CF_3)_2-$, $J_{C-F} = 290$ Hz), 122.29 (quartet, $-C(CF_3)_2OCH_2-$, $J_{C-F} = 293$ Hz), 93.95 ($-OCH_2O-$), 85.27 (septet, $-C({=}O)OC(CF_3)_2-$, $J_{C-C-F} = 28$ Hz), 82.84 (septet, $-C(CF_3)_2OCH_2O$, $J_{C-C-F} = 27$ Hz), 57.13 ($-OCH_3$), 34.48 (methine *C* adjacent to ester), 34.29 (methine *C* adjacent to ether), 24.02 (methylene *C* adjacent to ester), 21.66 (methylene *C* adjacent to ether); ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ −68.51.

Synthesis of 2-[4-(2,2,2-Trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)]styrene (4). 4-(2-Hydroxyhexafluoroisopropyl)styrene was synthesized using a modified procedure reported by Snow et al.[19] The protection reaction of a hydroxyl group was carried out using chloromethyl ethyl ether as described for **3**: ^1H NMR($CDCl_3$, 400 MHz): δ 7.52 (q, 4H, aromatic), 6.72 (q, 1H, $CH_2{=}CH-$), 5.82 (d, 1H, $CHH_{cis}{=}CH-$

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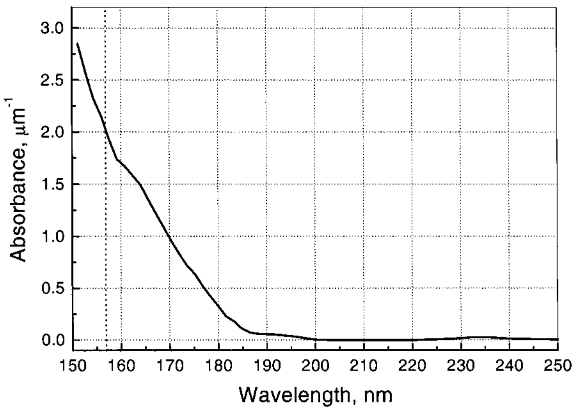


Figure 1. VUV-VASE spectrum of poly(**2**).

), 5.35 (d, 1H, $CHH_{trans}{=}CH{-}$), 4.87 (s, 2H, $-OCH_2O-$), 3.79 (q, 2H, $-OCH_2CH_3$, $J = 7$ Hz), 1.25 (t, 3H, $-OCH_2CH_3$, $J = 7$ Hz); ^{13}C NMR($CDCl_3$, 100 MHz): δ 139.53, 128.50, 127.41, and 126.44 (aromatic *C*), 135.62 ($CH_2{=}CH-$), 122.41 (quartet, $-CF_3$, $J_{C-F} = 288$ Hz), 116.06 ($CH_2{=}CH-$), 92.49 ($-OCH_2O-$), 82.20 (septet, $-C(CF_3)_2-$, $J_{C-C-F} = 29$ Hz), 65.50 ($-OCH_2CH_3$), 14.98 ($-OCH_2CH_3$).

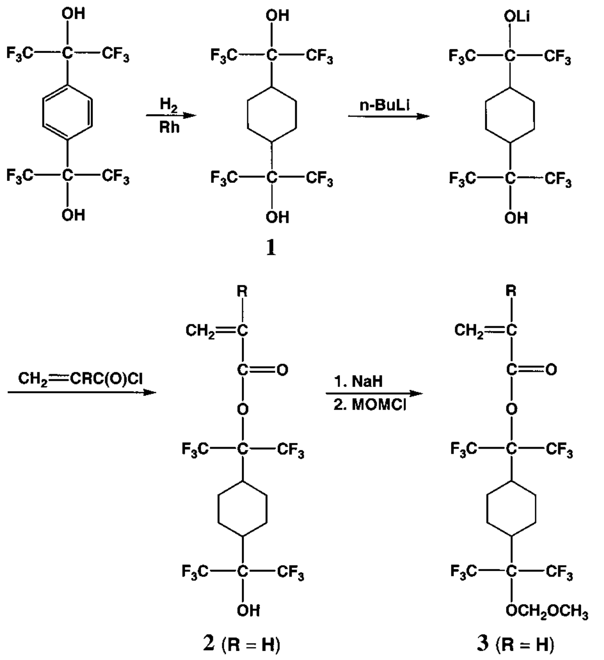
Polymerization. Radical polymerization of HFIPA-functionalized monomers was carried out using 2,2′-azobisisobutyronitrile (AIBN) in THF at 70 °C. The calculated amounts of monomers, solvent, and initiator were charged into the polymerization tubes, which were then immersed in a Dewar flask containing liquid nitrogen. After three cycles of freeze−thaw treatment under N_2, the tubes were sealed and placed in an oil bath at 70 °C for 24 h. Polymers were recovered by precipitation into distilled water twice and dried in a vacuum at 50 °C.

Lithographic Evaluation. Imaging experiments at 248 nm were carried out using a Nikon 248 nm stepper ($NA = 0.42$ and $\sigma = 0.5$) equipped with a KrF excimer laser (Cymer CX-2LS). Copolymers were dissolved in propylene glycol methyl ether acetate (PGMEA) (~15 wt %), and to this was added triphenylsulfonium perfluoro-1-butanesulfonate, dissolved in PGMEA, as a photoacid generator (PAG) in 1−5 wt % with respect to the polymer weight. Trioctylamine (TOA) or tetrabutylammonium hydroxide (TBAH) was added to the solution as a base to prevent acid diffusion in unexposed areas. The resist solution was filtered through a 0.2 μm membrane filter and spin-coated onto silicon wafers either primed with HMDS gas or treated with antireflective coatings. Postapply bake (PAB) was carried out at 90~115 °C for 60~90 s. Postexposure bake (PEB) was carried out at 90~130 °C for 60~90 s, and development was conducted for 20~60 s in 0.262 N tetramethylammonium hydroxide (TMAH) solution. The film thickness was measured on a Tenkor P-10 Surface Profiler, and developed patterns were imaged with a Leo 982 (Zeiss) scanning electron microscope (SEM). Imaging experiments at 157 nm were carried out at International SEMATECH using an Exitech 157 nm Microstepper ($NA = 0.6$ and $\sigma = 0.7$).

Results and Discussion

Tailoring Transparency of Polyacrylates at 157 nm. Our strategy to prepare highly transparent resist platforms at 157 nm involves the incorporation of a highly fluorinated building block, 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane (**1**), that has two HFIPA functional groups, into various acrylic monomers as shown in Scheme 1. This scheme allows the straightforward synthesis of various HFIPA-containing acrylic monomers where R is H, CH_3, F, or CF_3 using a corresponding acid chloride. The highly fluorinated building block, **1**, was prepared by simple hydrogenation of 1,4-bis(2-hydroxyhexafluoroisopropyl)benzene using a supported rhodium catalyst (5 wt % on carbon powder).[18] To minimize the formation of diacrylate, lithium alkoxide was prepared as an intermediate by lithiation of **1** using *n*-buyllithium. With the use of Scheme 1, ~50% yield was obtained on the basis of **1**, and the product separated by column chromatography included 52.2 mol % of **2** (R = H), 15.5 mol % of diacrylate, and 32.3 mol % of **1**. The protection reaction of the HFIPA group in monomer **2** was carried out using methoxymethyl chloride to yield monomer **3** (R = H) with an acid labile methoxy methyl group.

Scheme 1



To examine the effect of a fluoroalkyl group on the absorbance of the acrylic backbone, monomer **2** was polymerized by simple radical polymerization and the absorbance of the resulting poly(**2**) was measured using VUV-VASE. As shown in Figure 1, poly(**2**) exhibited unusually high transparency at 157 nm and the absorbance at this wavelength was found to be 1.93 μm^{-1}. Although this is the lowest absorbance value reported for polyacrylates, further decrease in absorbance can be easily achieved by replacing the α-hydrogen in poly(**2**) with an α-fluorine or an α-trifluoromethyl group. Since Willson et al. reported that poly(methyl α-triflurom-ethylacrylate) exhibits an absorbance of ~2.7 μm^{-1} at 157 nm,[10] it is expected that further tailoring of the transparency of poly(**2**) is available by incorporation of an α-trifluoromethyl group.

The unusual transparency of poly(**2**) may be accounted for in terms of the electronic structure of the carboxyl group as well as the volume effect of the trifluoromethyl group. The effect on the electronic structure of the carboxyl group of geminal trifluoromethyl groups, incorporated in the β-position to the acrylate ester oxygen, can be readily seen from ^{13}C NMR spectroscopy. While the chemical shifts of carboxyl carbons in poly[alkyl (meth)acrylate)]s are observed at

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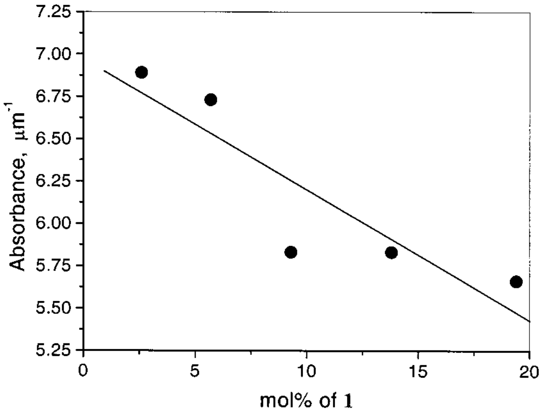

Figure 2. Absorbance of PMMA at 157 nm with various mol % of **1** with respect to the PMMA repeating unit.

~175 ppm, the carboxyl carbon in poly(**2**) exhibits an upfield shift by ~5 ppm and the chemical shift is observed at ~170 ppm. This indicates that the geminal CF_3 group in the β-position to the acrylate ester oxygen induces significant changes in the electronic structure of the carboxyl carbon in poly(**2**), rendering the carbonyl chromophore less absorbing than expected at 157 nm.

The van der Waals volume of the CF_3 group was reported to be 42.6 Å^3, and this is considerably larger than that of the CH_3 group which is 16.8 Å^3.[20] Therefore, one can imagine that, with poly(**2**), the concentration of the ester group per unit volume is significantly diluted in the presence of four bulky CF_3 groups. To examine the volume effect of the CF_3 group on the absorbance of acrylic backbones, the transparent building block, **1**, was mixed with poly(methyl methacrylate) (PMMA) and the absorbance was measured using VUV-VASE. Figure 2 shows the absorbance of PMMA at 157 nm with various mol % of **1** with respect to the PMMA repeating unit. If 50 mol % of **1** is mixed with PMMA, we can construct an imaginary polymer structure that has a chemical formula of poly(**2**) with extra C_2H_8O elements per repeating unit. From the linear fit of the data in Figure 2, it is calculated that this imaginary polymer has an absorbance of 3.11 μm^{-1} at 157 nm, and a further decrease in absorbance can be expected by removing the extra C_2H_8O elements per repeating unit. This estimation indicates that the volume effect of the bulky CF_3 group cannot be ruled out in the explanation of the high transparency of poly(**2**). It is also notable that fluorocarbinol-containing small molecules, such as **1**, can be used as transparent dissolution inhibitors after protection with acid-labile groups.

Chemically Amplified Acrylic Resist Functionalized with HFIPA. The synthesis of chemically amplified resists for 157 nm lithography was carried out by copolymerization of monomer **2** with monomer **3** which has an acid-labile protecting group. Although it remains to be proven, Scheme 2 is proposed for the chemical amplification of the methoxy methyl protecting group in the presence of a PAG. The methoxy methyl cation has been reported to possess large gaseous stabilization energy of 68 kcal, which is very close to 74 kcal for a *tert*-butyl cation which is one of the most common intermediates generated in the lithographic process with chemically amplified resist systems.[21] It appears that one of the possible pathways for the chemical amplification, i.e., the acid-catalyzed deprotection, is through the hydrolysis of the carbenium ion by adventitious moisture as shown in Scheme 2.[22]

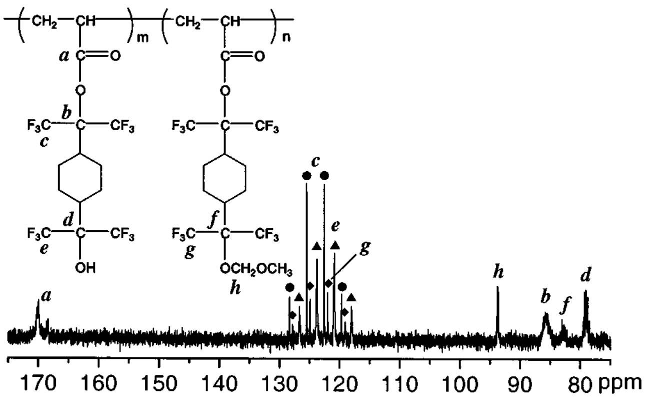

Figure 3. Expanded ^{13}C NMR (100 MHz, acetone-d_6) spectrum of poly(**2**-*co*-**3**) with 28 mol % of **3**.

Scheme 2

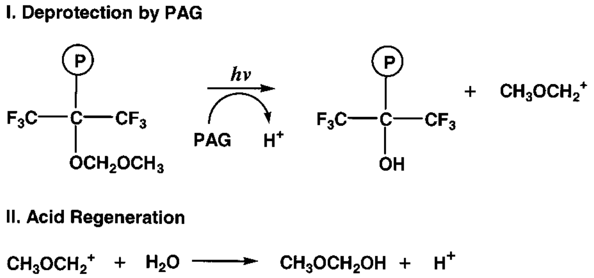

Figure 3 shows the expanded ^{13}C NMR spectrum of poly(**2**-*co*-**3**) with structural assignments. The trifluoromethyl carbon splits into quartet at ~123 ppm with J_{C-F} = 288 Hz, and three sets of quartet (*c*, *e*, and *f*) are observed in Figure 3. As discussed earlier, the chemical shifts of carboxyl carbon exhibit a significant upfield shift compared to those of carboxyl carbons in poly[alkyl (meth)acrylate]s. Chemical shifts of carboxyl carbon corresponding to racemic triads (rr) are observed at 169.98 ppm and meso triads (mr) are observed at 168.41 ppm. This result indicates that radical copolymerization of **2** and **3** yields syndiotatic-rich poly(**2**-*co*-**3**).

Thermal stability of poly(**2**-*co*-**3**) was studied using TGA. The TGA traces of poly(**2**-*co*-**3**), with 28 mol % of protected monomer **3**, are shown in Figure 4. While Figure 4A shows TGA traces of poly(**2**-*co*-**3**) with an onset temperature of 336 °C for decomposition, Figure 4B shows those of poly(**2**-*co*-**3**) after exposure to 248 nm radiation in the presence of PAG. Although the corresponding weight loss for the protecting group (CH_3-OCH_2-) is not clear from Figure 4B, most probably due to its very low weight content (~2.6 wt %), it should be noted that poly(**2**-*co*-**3**) exhibits remarkable thermal stability, even in the presence of photodecomposed acid, compared to conventional acrylic resists which have poor thermal stability with onset temperatures for decomposition at ~200 °C.[21] This excellent thermal

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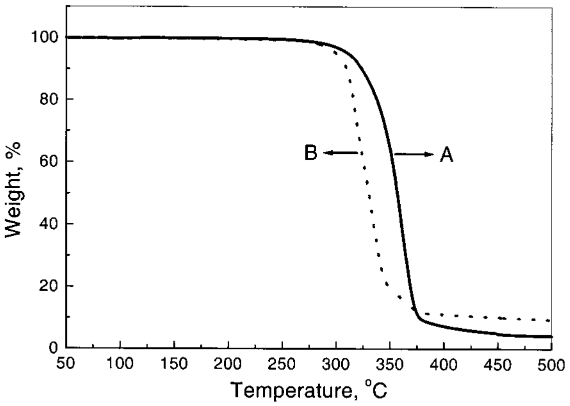


Figure 4. TGA traces of poly(**2**-*co*-**3**) before (A) and after exposure to 248 nm in the presence of PAG (B).

stability can be ascribed to the presence of the pure acrylic backbone without methyl substitution at the α-position.[24]

Lithographic performances of poly(**2**-*co*-**3**), with 28 mol % of protected monomer **3**, were tested using a 248 nm stepper. Although the resist film exhibited clear latent images after exposure at 248 nm followed by postexposure bake (PEB), imaging was not successful after development in 0.262 N TMAH solution. While poly(**2**) exhibited good wetting properties on a HMDS vapor-primed silicone wafer, poly(**2**-*co*-**3**) exhibited relatively poor wettability most probably due to its nonpolar nature after partial protection with a methoxy methyl group. Attempted development in 0.262 N TMAH solution containing various amounts of isopropyl alcohol was less than satisfactory, and the resist exhibited poor adhesion properties even with a small percent of isopropyl alcohol in 0.262 N TMAH solution. It appears that, although HFIPA alone was successfully demonstrated by Przybilla as an acidic functional group,[7] it is necessary to incorporate a more acidic functional group to achieve high contrasts resulting from enhanced dissolution selectivity between exposed and unexposed areas.

Hybrid Resists Containing Conventional Imaging Groups. To develop resist systems with high contrast, we extended our studies to hybrid resist systems which are copolymers of **2** with conventional methacrylic monomers commonly used in the 193 nm resist design. With these hybrid resists, imaging mechanism is achieved by the deprotection of methacrylates and HFIPA is used as a transparent acidic adjuvant. By this strategy, while achieving high contrasts, we can also avoid resist swelling problems, often encountered with resist systems containing (meth)acrylic acid, in unexposed areas due to much less acidity of HFIPA than those of (meth)acrylic acids. Since the hybrid systems are expected to have lower transparency than pure HFIPA systems, it was of great interest to examine the effect of protected methacrylic comonomers on the transparencies of the resulting hybrid systems. For the transparency studies, a series of copolymers of monomer **2** with *tert*-butyl or tetrahydropyranyl methacrylate were prepared by radical polymerization. Surprisingly, only a modest deterioration in transparency was observed with hybrid systems containing 10~40 mol % methacrylic comonomers. In Figure 5 are shown VUV-VASE spectra of hybrid copolymers obtained using 30 and 40 mol % of tetrahydropyranyl methacrylate (THPMA) in the copolymerization. With 30 mol % of THPMA, the hybrid system exhibits an absorbance of 2.22 μm^{-1} at 157 nm, and nominal increase in absorbance is observed with 40 mol % of THPMA (2.38 μm^{-1} at 157 nm). This again clearly demonstrates that the volume effect of the CF_3 group plays an important role in the transparency of the hybrid systems.

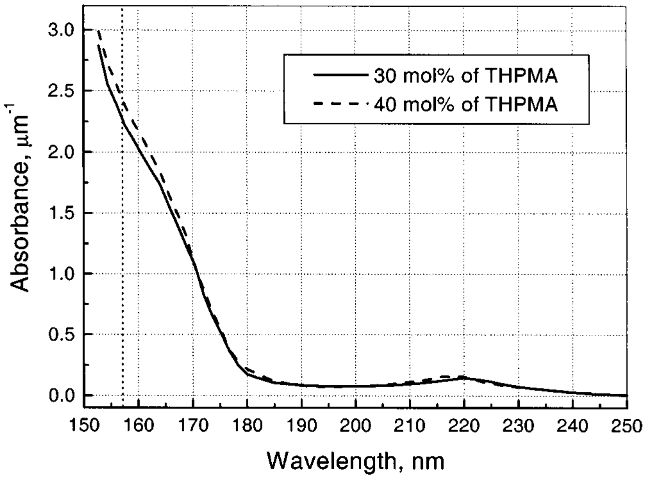
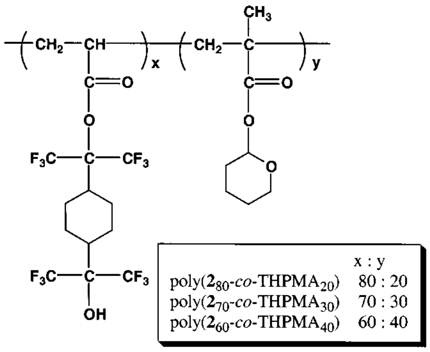


Figure 5. VUV-VASE spectra of hybrid copolymers, poly(**2**-*co*-THPMA), obtained using 30 and 40 mol % of **4** in the copolymerization feed.



	x : y
poly(2_{80}-*co*-THPMA$_{20}$)	80 : 20
poly(2_{70}-*co*-THPMA$_{30}$)	70 : 30
poly(2_{60}-*co*-THPMA$_{40}$)	60 : 40

Figure 6. Structures of poly(**2**-*co*-THPMA) resists and their copolymerization feed ratios.

Encouraged by the transparency data of the hybrid systems, three poly(**2**-*co*-THPMA)-based platforms were prepared with various amounts of THPMA and their structures and copolymerization feed ratios are shown in Figure 6. Thermal stability of these hybrid systems was examined using TGA, and their TGA traces are shown in Figure 7. As can be seen in Figure 7, poly(**2**-*co*-THPMA)-based platforms exhibit three distinct steps during thermal decomposition. The first onset temperature for decomposition is observed at ~140 °C, and this is ascribed to the presence of tetrahydropyranyl ether which has relatively lower activation energy for decomposition compared to the *tert*-alkyl protecting groups commonly used in acrylic resists.[25] The presence of second and third steps in decomposition can be assigned to the decomposition of methacrylic structures and

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(23) Nozaki, K.; Kaimoto, Y.; Takahashi, M.; Takechi, S.; Abe, N. *Chem. Mater.* **1994**, *6*, 1492.

(24) Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *24*, 4017.

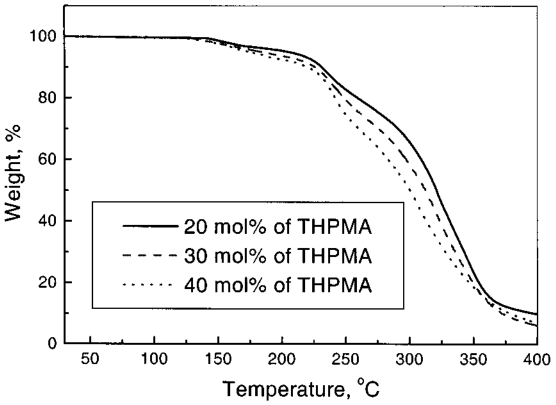

Figure 7. TGA traces of poly(**2**-*co*-THPMA)-based resist platforms.

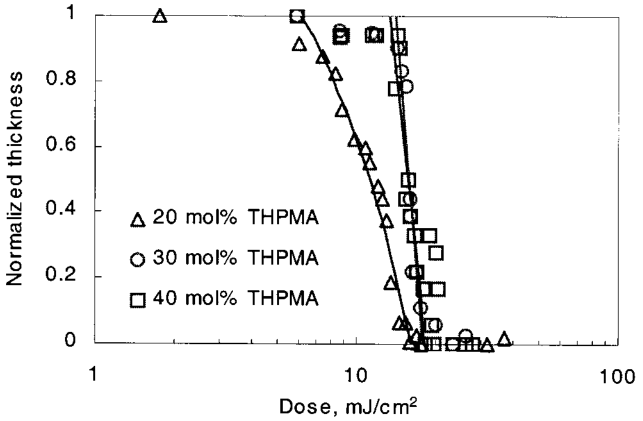

Figure 8. Contrast curves obtained with poly(**2**-*co*-THPMA)-based resists in the presence of 1 wt % PAG; processing conditions include PAB at 115 °C for 60 s, PEB at 90 °C for 60 s, and development in 0.262 N TMAH for 60 s.

thermally stable fluorinated acrylic structures, respectively.[24]

Lithographic Evaluation of Hybrid Resists. In contrast to poly(**2**-*co*-**3**) which contains only HFIPA as an acidic group, poly(**2**-*co*-THPMA)-based resists exhibited excellent spin qualities on a HMDS-primed silicone wafer. Process optimization was carried out by varying PEB temperature with fixed PAB temperature of 115 °C, and best results were obtained with PEB temperature of 90 °C. We also studied the effect of base additives, which are used to control acid diffusion into unexposed areas, on the lithographic performances of poly(**2**-*co*-THPMA)-based resists. In general, the addition of base additives into poly(**2**-*co*-THPMA)-based resists improved the lithographic performances, and therefore, 2 wt % TOA, with respect to the weight of PAG, was added to the resist formulation. To minimize additional increases in absorbance due to the presence of PAG, lithographic evaluation on a 248 nm stepper was carried out in the presence of 1 wt % PAG. In Figure 8 are shown contrast curves obtained with three hybrid resists containing different amounts of THPMA. While poly($\mathbf{2}_{80}$-*co*-THPMA_{20}) exhibited much lower sensitivity or slower dose response, hybrid resists obtained with 30 and 40 mol % THPMA exhibited sharp contrast with a clearing dose of ~18 mJ/cm².

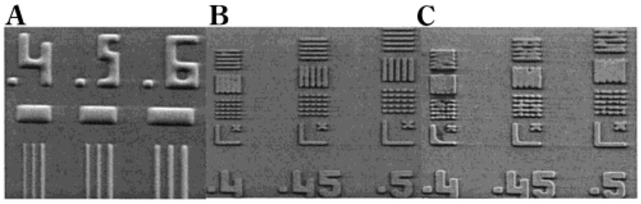

Figure 9. SEM images obtained with poly($\mathbf{2}_{80}$-*co*-THPMA_{20}) (A), poly($\mathbf{2}_{70}$-*co*-THPMA_{30}) (B), and poly($\mathbf{2}_{60}$-*co*-THPMA_{40}) (C) using processing conditions listed in Figure 8.

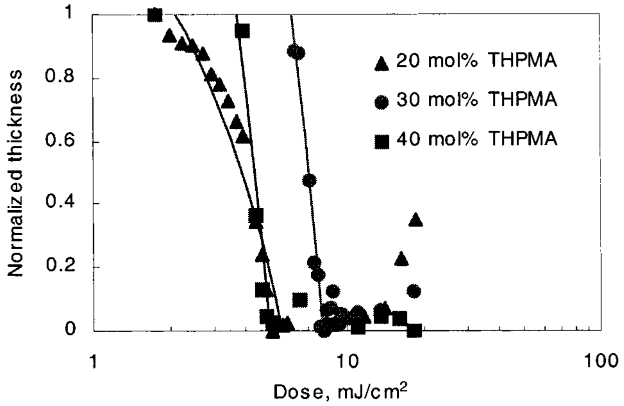

Figure 10. Contrast curves obtained with poly(**2**-*co*-THPMA)-based resists in the presence of 3 wt % PAG; other processing parameters are the same as listed in Figure 8.

In Figure 9 are shown SEM images obtained with poly(**2**-*co*-THPMA)-based resists in the presence of 1 wt % PAG. While severe top-rounding was observed with poly($\mathbf{2}_{80}$-*co*-THPMA_{20}), only partial resolution was achieved with poly($\mathbf{2}_{70}$-*co*-THPMA_{30}) and poly($\mathbf{2}_{60}$-*co*-THPMA_{40}) when the feature sizes were below 500 nm. It is notable that poly($\mathbf{2}_{70}$-*co*-THPMA_{30}) gives better resolution than poly($\mathbf{2}_{60}$-*co*-THPMA_{40}). For example, with poly($\mathbf{2}_{70}$-*co*-THPMA_{30}), isolated lines are clearly resolved down to 400 nm and horizontal dense lines are resolved down to 450 nm. With poly($\mathbf{2}_{60}$-*co*-THPMA_{40}), however, only isolated lines bigger than 400 nm were resolved like the example shown in Figure 9. Since these results indicate that poly($\mathbf{2}_{70}$-*co*-THPMA_{30}) forms more acidic exposed areas than poly($\mathbf{2}_{60}$-*co*-THPMA_{40}), it is concluded that poly($\mathbf{2}_{60}$-*co*-THPMA_{40}) undergoes less than complete acid-catalyzed deprotection under given conditions.

In the next series of experiments, 3 wt % PAG was employed in the formulation with three hybrid systems and imaging experiments were carried out without changing other processing parameters. Figure 10 shows contrast curves obtained with 3 wt % PAG. Under these conditions, three hybrid systems exhibited clearing doses much lower than those with 1 wt % PAG and poly($\mathbf{2}_{60}$-*co*-THPMA_{40}) exhibited a decrease in the clearing dose by a factor of ~3 compared to the previous result with 1 wt % PAG. Although it is difficult to explain the relatively low clearing dose with poly($\mathbf{2}_{80}$-*co*-THPMA_{20}), the lower clearing dose with poly($\mathbf{2}_{60}$-*co*-THPMA_{40}) than with poly($\mathbf{2}_{70}$-*co*-THPMA_{30}) clearly indicates that the former undergoes acid-catalyzed deprotection more efficiently with 3 wt % PAG.

SEM images obtained in the presence of 3 wt % PAG are shown in Figure 11, and dramatic improvement in lithographic performances was achieved in terms of

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(25) Taylor, G. N.; Stillwagon, L. E.; Houlihan, F. M.; Wolf, T. M.; Sogah, D. Y.; Hertler, W. R. *Chem. Mater.* **1991**, *3*, 1031.

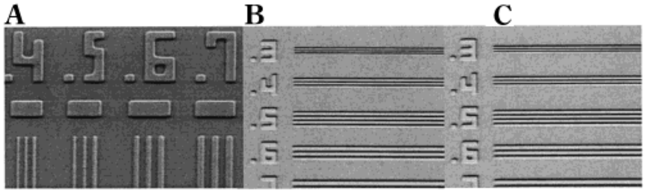

Figure 11. SEM images obtained with poly($\mathbf{2}_{80}$-*co*-THPMA$_{20}$) (A), poly($\mathbf{2}_{70}$-*co*-THPMA$_{30}$) (B), and poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$): other processing conditions are the same as listed in Figure 8.

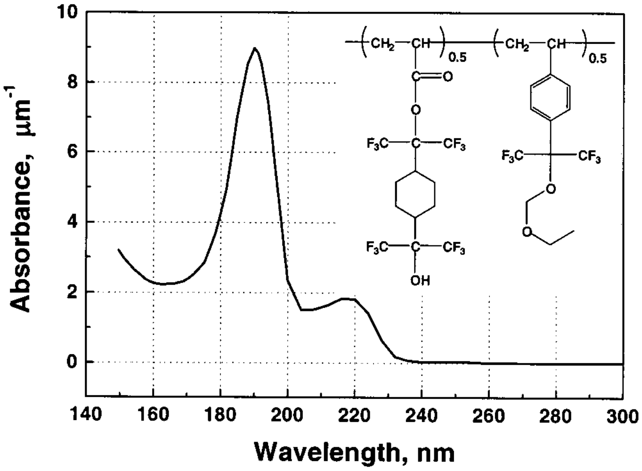

Figure 12. VUV-VASE spectrum of poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$).

resolution and photospeeds. While SEM images in Figure 9 were obtained with exposure doses of ~20 mJ/cm^2, doses less than ~9 mJ/cm^2 were enough to print SEM images with much better exposure latitude. Top-rounding was significantly alleviated with poly($\mathbf{2}_{80}$-*co*-THPMA$_{20}$), and dense lines were resolved down to 300 nm with poly($\mathbf{2}_{70}$-*co*-THPMA$_{30}$) and poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$). Although a lower dose was required with poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$), similar lithographic performances were achieved with poly($\mathbf{2}_{70}$-*co*-THPMA$_{30}$) and poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$) in terms of resolution.

Use of 248 nm Resist Backbones for 157 nm Lithography. Lithographic studies with poly(**2**-*co*-THPMA)-based resists clearly demonstrated that, by incorporation of a transparent building block, acrylic backbones can be used as resist platforms for 157 nm lithography. Although dry etch resistance can be imparted to the poly(**2**-*co*-THPMA)-based resists by replacing both cyclohexyl and tetrahydropyranyl groups with alicyclic structures as demonstrated by Nozaki et al. in the design of 193 nm resists with methacrylic backbones,[23] this approach may require a compromise with loss in transparency due to the additional absorbance by the alicyclic group. Therefore, in an effort to find comonomers that are not only etch resistant but also transparent at 157 nm, we embarked on the study of modified styrenic monomers. Preliminary studies with silylated polystyrenes indicated that the transparency of even polystyrenic backbones can be significantly improved by incorporation of alkyl silyl groups in the para position. For example, the absorbance of poly(*p*-trimethylsilyl styrene) was measured to be 4.37 μm^{-1} at 157 nm and this is significantly lower than that of polystyrene (~6 μm^{-1}). From this result, one can expect that, by combination of monomer **2** with modified styrenic monomers, the use of backbones used in 248 nm resists, known arguably as the best chemically amplified resists, is possible for 157 nm lithography.

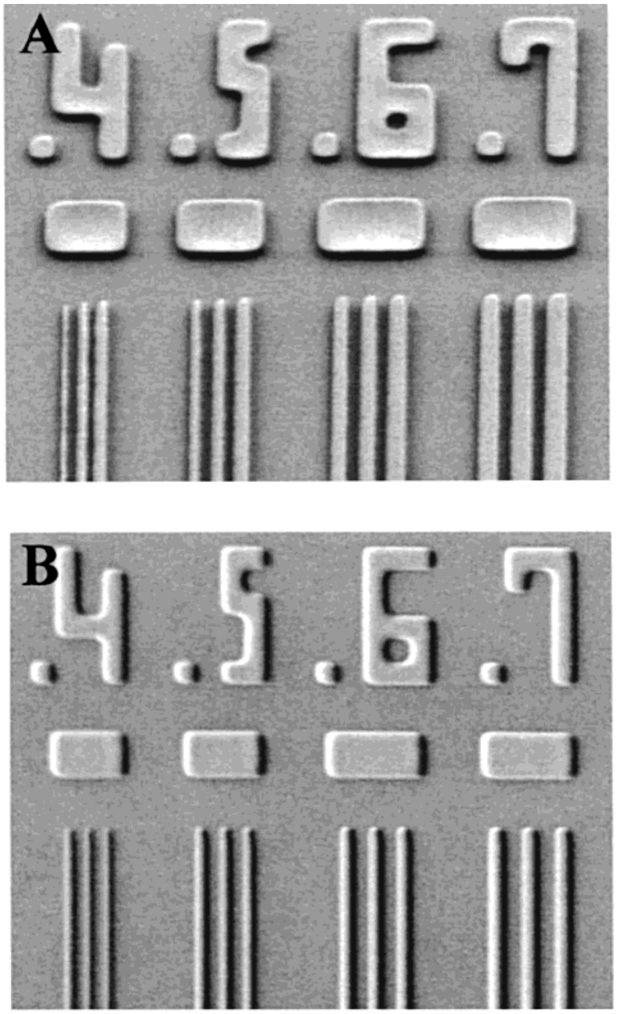

Figure 13. SEM images obtained with poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$): processing conditions include (A) PAB at 115 °C for 90 s, PEB at 115 °C for 90 s, and development in 0.262 N TMAH for 3 min and (B) PAB at 125 °C for 90 s, PEB at 100 °C for 60 s, and development in 0.262 N TMAH for 5 min.

This strategy was implemented in the synthesis of copolymers of **2** with HFIPA-functionalized styrene. As an imageable monomer, 2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)]styrene (**4**) was prepared by protecting HFIPA-functionalized styrene, 4-(2-hydroxyhexafluoroisopropyl)styrene, with ethoxy methyl chloride. In Figure 12 is shown a VUV-VASE spectrum of poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$), which was obtained with 50 mol % of **4** in the copolymerization feed, and the absorbance at 157 nm was measured to be 2.38 μm^{-1}. This clearly demonstrates that by judicious modification of strongly absorbing chromophores, such as carbonyl or aromatic groups, it is possible to use conventional resist backbones in the design of chemically amplified resists for 157 nm lithography.

It is also interesting to note that poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$) is ultratransparent at 248 nm, displaying an absorbance of ~0.07 μm^{-1} at this wavelength, which is significantly lower than those of commercial resists for 248 nm lithography. This can be attributed to the presence of a hexafluoroisopropyl group in monomer **4** as well as the high transmittance of a fluorocarbinol-containing acrylic

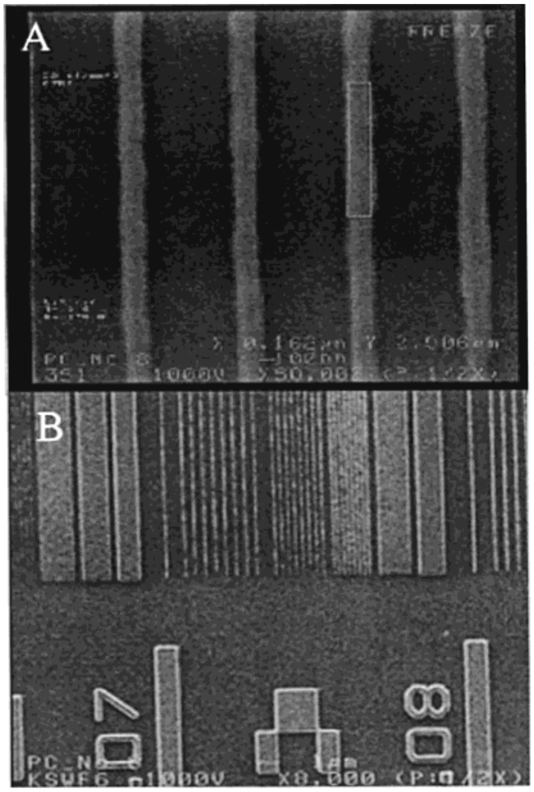

Figure 14. SEM images obtained with poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$): processing conditions include (A) PAB at 100 °C for 60 s, PEB at 90 °C for 90 s, and development in 0.263 N TMAH for 20 s and (B) PAB at 90 °C for 60 s, PEB at 90 °C for 90 s, and development in 0.263 N TMAH for 20 s.

backbone that exhibits an absorbance less than 0.01 μm^{-1} at 248 nm. Therefore, this type of a resist backbone can also be used for 248 nm lithography, especially in a process where features with high aspect ratios are required.

Imaging experiments were carried out with poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$) using a 248 nm stepper. Figure 13 shows representative SEM images obtained by using two different processing conditions. Two extreme results, underexposed (Figure 13A) and overexposed images (Figure 13B), were obtained under given conditions, and optimization could not be achieved. Compared to the hybrid resists which generate more acidic exposed areas, poly($\mathbf{2}_{50}$-*co*-$\mathbf{4}_{50}$) required much higher energy (>30 mJ/cm^2) as well as longer development time (3~5 min) to print these images. Although this may be attributed to the presence of ethoxy methyl ether that has higher activation energy for deprotection compared to tetrahydropyranyl ether, the more important factor would be the lower acidity of HFIPA than methacrylic acid. This again clearly demonstrates that HFIPA alone is not a good acidic group and, to achieve high contrasts, it is necessary to incorporate more acidic components in the resist backbone. It is expected that, by using HFIPA as a transparent and acidic adjuvant, lithographic performances can be enhanced by simple terpolymerization of **2** and **4** (or unprotected HFIPA-substituted styrene) with any (meth)acrylate monomers protected with an acid-labile group.

Lithography at 157 nm. In parallel with imaging experiments at 248 nm, lithographic evaluation at 157 nm was also carried out with poly(**2**-*co*-THPMA)-based resists. In Figure 14 are shown SEM images obtained with poly($\mathbf{2}_{80}$-*co*-THPMA$_{20}$) and poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$) using conventional illumination. Figure 14A was imaged in the presence of 6 wt % PAG and 0.3 wt % TBAH and clearly demonstrates 130 nm 1:5 line and space patterns. Figure 14B was obtained in the presence of 5 wt % PAG and 0.3 wt % TBAH, and isolated lines were resolved down to 80 nm with poly($\mathbf{2}_{60}$-*co*-THPMA$_{40}$). It is expected that further miniaturization in feature sizes is possible using resolution enhancement techniques.

Conclusions

It was found that fluorocarbinol-modified acrylic and styrenic monomers can be used in the design of chemically amplified photoresists, highly transparent at 157 nm. Improvement in transparency was also achieved by adding a transparent building block, **1**, to highly absorbing acrylates, such as PMMA. This result demonstrates that fluorocarbinol-containing small molecules can be used as transparent dissolution inhibitors after protection with acid-labile groups. Preliminary results in 157 nm lithography proved that, with judicious molecular-level design, the synthesis of single-layer resists for 157 nm lithography is possible using simple chemistries.

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