

New Photoresist Materials for 157-nm Lithography. Poly[Vinylsulfonyl Fluoride-*co*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-styrene] Partially Protected with *tert*-Butoxycarbonyl

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Our molecular orbital calculations predicted excellent transparencies of molecules having sulfonyl fluoride groups in the vacuum ultraviolet (VUV) region. An optical density (OD) measurement of poly(vinylsulfonyl fluoride) [poly(VSF)] prepared by free radical polymerization of VSF clearly supported this calculation (OD = 2.1 μm^{-1} at 157 nm). A new copolymer, poly[(VSF)₄₀-*co*-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene (HF1St)₆₀] [poly(VSF₄₀-*co*-HF1St₆₀)] prepared by free radical copolymerization of VSF and HF1St showed good transparency (OD = 2.4 μm^{-1}) as well. Poly(VSF₄₀-*co*-HF1St₂₂-*co*-*tert*-butoxycarbonyl HF1St₃₈) (OD = 2.8 μm^{-1}) was prepared from poly(VSF₄₀-*co*-HF1St₆₀) and di-*tert*-butyl dicarbonate in the presence of 4-(dimethylamino)pyridine (DMAP). A resist film consisting of poly(VSF₄₀-*co*-HF1St₂₂-*co*-*tert*-Boc HF1St₃₈) and 5 wt % triphenylsulfonium triflate showed a sensitivity of 7.2 mJ cm^{-2} and a contrast of 3.1 when a 150-nm-thick film prebaked at 100 °C for 1 min was exposed to 157-nm laser, postbaked at 130 °C for 1 min, and developed with a 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution.

Introduction

Optical lithography continues to extend its resolution limit and may reach the 65-nm node using a 157-nm technology.¹ The problem is that most common lithographic materials, including commercial photoresists, strongly absorb the 157-nm radiation. The design of materials satisfying all of the requirements for single-layer photoresists at 157 nm is a formidable challenge.

Initial systematic investigations by Kunz et al.^{2,3} indicated that siloxane/silsesquioxane backbone polymers and highly fluorinated polymers are sufficiently transparent in this region to be considered possible candidate platforms for new resists. Based on this study, poly(methyl α -trifluoromethylacrylate),^{4,5} poly[4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene] poly-(HF1St),^{6,7} poly[5-(2-trifluoromethyl-1,1,1-trifluoro-2-

hydroxypropyl)-2-norbornene]^{8–10}, and other fluorinated polymers^{11–28} have been reported as single-layer photoresists for 157-nm lithography.

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Matsuzawa et al. have reported quantum chemical methods to calculate the absorption spectra of molecules in the vacuum ultraviolet (VUV) region.^{29–32} In their calculations, however, the transition energies of the molecules have been adjusted using empirical equations. In a preceding paper, we have reported that time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional with the 6-311++G(d,p) basis set is a very useful tool to predict the transparency of molecules in the VUV region, and in particular, useful for the design of photoresist materials for F₂ lithography.^{33,41} No empirical corrections were incorporated in the calculations. With the help of this method, we surveyed many polymers and found that poly(vinylsulfonyl fluoride) [poly(VSF)] possesses high transparency in the 157-nm region. During the preparation of this manuscript, the near UV photoactive diazonaphthoquinone containing a sulfonate group have been found to be quite transparent at 157 nm and employed in nonchemically amplified 157-nm resist formulation.³⁴

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In this paper, we report a novel resist system based on partially *tert*-butoxycarbonyl (*tert*-BOC)-protected poly[VSF-*co*-(HF1St)] and triphenylsulfonium triflate as a photoacid generator (PAG) as an attractive single-layer 157-nm photoresist.

Experimental Section

Materials. 4-Chlorostyrene was distilled from CaH₂. Tetrahydrofuran (THF) was dried over sodium, distilled twice, and used immediately. α,α' -Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Other reagents were purchased and used as received. Column chromatography was carried out using silica gel 60 (Merck 0.063–0.200 mm).

Caution! 2-Chloroethanesulfonyl chloride, 2-chloroethanesulfonyl fluoride, and ethenesulfonyl fluoride are severe eye and skin irritants. Systemic toxic effects may result from skin adsorption and exposure to vapors. Exposure to liquid and vapor should be avoided by use of adequate ventilation and appropriate protective clothing.

Synthesis of 2-Chloroethanesulfonyl Chloride. Powdered phosphorus pentachloride (400 g, 1.9 mol) and sodium isethionate (118 g, 0.80 mol) dehydrated at 130 °C in *vacuo* for 4 h were mixed, and the resulting solution was refluxed at 135 °C for 6 h. The solution was cooled to room temperature, poured on ice (ca 2 kg), and stirred in ice–water until phosphoryl chloride had completely reacted with water. The separated oil was extracted with toluene and dried over calcium chloride. After evaporation of toluene, 2-chloroethanesulfonyl chloride was distilled as colorless oil. Yield 120 g (92%). bp 80–81 °C/10 mmHg (lit. 80–82 °C/10 mmHg).³⁵

IR (KBr): ν 2992, 2935 (–CH₂), 1376 (–SO₂Cl) cm^{−1}. ¹H NMR (300 MHz, CDCl₃): δ 3.97–4.10 (m, 4H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 35.9, 66.2 ppm.

Synthesis of 2-Chloroethanesulfonyl Fluoride. A solution of potassium fluoride (33.6 g, 0.58 mol) in water (67 mL) was added dropwise at 25 °C to a solution of 2-chloroethanesulfonyl chloride (48 g, 0.29 mol) in THF (120 mL). The mixture was stirred for 2 h, and then water (50 mL) was added. The organic phase was separated and the aqueous phase was extracted with ether. The combined solution was dried over anhydrous magnesium sulfate and then distilled under reduced pressure to give the desired product as a colorless oil. Yield 35 g (71%). bp 93–95 °C/50 mmHg.

IR (KBr): ν 1411 (–SO₂F) cm^{−1}. ¹H NMR (300 MHz, CDCl₃): δ 3.7–3.8 (m, 2H, CH₂), 3.9–4.0 (m, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 35.6, 53.2 (*J* = 18.45 Hz) ppm.

Synthesis of Vinylsulfonyl Fluoride (VSF). To a rapidly stirred mixture of 2-chloroethanesulfonyl fluoride (22 g, 0.15 mol) and water (50 mL) was added MgO (40 g) in portions at such a rate that the temperature of the mixture did not exceed 35 °C. Stirring was continued for 6 h after addition, and the organic layer was separated and dried over anhydrous magnesium sulfate. Vacuum distillation gave the desired compound as a colorless liquid. Yield 11 g (67%). bp 53–54 °C/70 mmHg.

IR (KBr): ν 1407 (–SO₂F) cm^{−1}. UV (CHCl₃): 273 nm. ¹H NMR (300 MHz, CDCl₃): δ 6.37–6.42 (m, 1H, CH), 6.65–6.80 (m, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 130.6 (*J* = 28.4 Hz) 134.9 (*J* = 12.0 Hz) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ 58.0 (m, SO₂F) ppm. Anal. Calc. for C₂H₃FO₂S: C, 21.82%; H, 2.75%; S, 29.12%. Found: C, 22.13%; H, 2.76%; S, 29.07%.

4-(1,1,3,3-Hexafluoro-2-hydroxypropyl)styrene (HF1St). A 500-mL three-neck flask equipped with a condenser and a three-way stopcock connected to a vacuum pump was evacuated and dried carefully with a heat gun, then flushed with nitrogen. Magnesium (8.0 g, 0.33 mol) was placed inside and activated in *vacuo* with vigorous stirring for 6 h. The system was maintained at 45 °C under nitrogen. THF (2 mL) and 1,2-dibromoethane (1.7 mL, 2 mmol) were added as an initiator. After the activation of magnesium, a solution of 4-chlorostyrene (41 g, 0.3 mol) dissolved in THF (250 mL) was added dropwise to the reaction flask at such a rate to maintain

gentle reflux. The reaction was refluxed for 1 h after all 4-chlorostyrene had been added. After the reaction was completed, the solution was poured into another three-neck flask (equipped with a coldfinger condenser, a three-way stopcock, and a rubber cap) which was previously dried with a heat gun and purged with nitrogen. Then, the rubber cap was replaced with a gas inlet tube connected to a 500-mL two-neck flask equipped with a dropping funnel. Trihydrous hexafluoroacetone (75 g, 0.34 mol) was added dropwise to sulfuric acid (300 mL) heated at 140 °C and an anhydrous hexafluoroacetone gas produced was introduced to a 4-vinylphenylmagnesium chloride solution at 0 °C. After addition of anhydrous hexafluoroacetone, the mixture was allowed to warm to room temperature and stirred for 2 h. The mixture turned dark brown. To this solution was slowly added a 6 mol/L HCl aqueous solution until the solution was clearly separated into two phases. The upper organic layer was separated and the aqueous layer was extracted three times with diethyl ether. The combined organic phases were washed with water, dried over magnesium sulfate, filtered, and concentrated on a rotary evaporator. The residue was purified by vacuum distillation and successive gradient column chromatography (SiO₂; hexane to dichloromethane) to give HF1St as a colorless liquid. Yield 64.0 g (74%). bp 40–45 °C/>1 mmHg.

IR (KBr): ν 3600 (–OH), 1211 (–CF₃) cm^{−1}. ¹H NMR (300 MHz, CDCl₃): δ 3.5 (s, 1H, OH), 5.3 (d, 1H, CH₂=, J = 11.1 Hz), 5.8 (d, 1H, CH₂=, J = 17.4 Hz), 6.7 (dd, 1H, =CH, J = 11.1 Hz, J = 17.5 Hz), 7.5 (d, 2H, Ar–H) 7.6 (d, 2H, Ar–H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 116.4, 123.2 (J = 285.7 Hz), 126.9, 127.3, 129.1, 136.3, 140.1 ppm. Anal. Calc. for C₁₁H₈F₆O: C, 48.90%; H, 2.98%; F, 42.19%. Found: C, 48.06%; H, 3.05%; F, 42.13%.

Poly(vinylsulfonyl fluoride) [Poly(VSF)]. VSF (0.22 g, 2 mmol) and AIBN (3.2 mg, 0.02 mmol) were charged into a polymerization tube, followed by several cycles of freeze and thaw. The tube was sealed and heated at 40 °C for 100 h. Then the tube was opened and the polymer was dissolved in acetone and purified by precipitation in diethyl ether twice. After purification, the polymer was dried under vacuum. M_n = 6100, M_w/M_n = 1.2, yield 0.116 g (53%).

¹H NMR (300 MHz, acetone-*d*₆): δ 2.6–3.2 (br, 2H, CH₂), 4.4–4.8 (br, 1H, CH) ppm. IR (KBr): ν 1403 (–SO₂F), 1203 (–SO₂F), 790 cm^{−1}.

Poly(HF1St). HF1St (0.54 g, 2 mmol) and AIBN (3.2 mg, 0.02 mmol) were charged into a polymerization tube followed by several cycles of freeze and thaw. The tube was sealed and heated at 60 °C for 24 h. The tube was opened, and then the polymer was dissolved in acetone and purified by precipitation in hexane twice and water once. After purification, the polymer was dried in vacuum. Yield 0.49 g (91%). White powder. M_n = 176 000. M_w/M_n = 2.2. Glass transition temperature (T_g) = 131 °C.

¹H NMR (300 MHz, acetone-*d*₆): δ 1.2–1.6 (br, 2H, CH₂), 2.9–3.2 (br, 2H, CH), 6.2–6.6 (br, 2H, aromatic), 7.2–7.6 (br, 2H, aromatic) ppm. IR (KBr): ν 3451 (–OH), 1272 (–CF₃), 1218 (–CF₃) cm^{−1}.

Poly(VSF-*co*-HF1St). VSF (0.11 g, 1 mmol), HF1St (0.27 g, 1 mmol), toluene (2 mL), and AIBN (3.2 mg, 0.02 mmol) were charged into a polymerization tube. Freeze–thaw cycles were repeated several times. The tube was sealed under vacuum and heated at 60 °C for 50 h. Then the tube was opened and the solvent was evaporated. The polymer was dissolved into acetone and was purified by precipitation in hexane twice and water once. After purification, the polymer was dried under vacuum. Yield 0.18 g (46%). White powder. M_n = 30 000. M_w/M_n = 1.5. T_g = 137 °C.

¹H NMR (300 MHz, acetone-*d*₆): δ 1.5–2.2 (br, CH₂), 2.8–3.0 (br, CH, CH₂), 4.4–4.8 (br, CH), 6.5–7.2 (br, aromatic), 7.4–7.8 (br, aromatic) ppm. IR (KBr): ν 3467 (–OH), 1403 (–SO₂F), 1218 (–CF₃) ppm. VSF: HF1St in copolymer was 26:74 determined by elemental analysis.

Measurements. FT-IR spectra were measured on a Horiba FT-720 spectrophotometer. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker DPX-300 spectrometer. Tetramethylsily-

lane was used as internal standard for ¹H and ¹³C NMR. For ¹⁹F NMR, fluorotrichloromethane was used as internal standard. Thermal analyses were performed on a Seiko SSS5000 TG-DTA 220 thermal analyzer at a heating rate of 10 °C min^{−1} for thermogravimetry (TG) and a Seiko SSS5000 DSC220 at a heating rate of 5 °C min^{−1} for differential scanning calorimetry (DSC) under a nitrogen atmosphere. The transmittance of resist films was measured with a F₂ laser exposure system VUVES-4500 (LithoTech Japan). VUV spectra were measured on a VUV-200 (JASCO). Gel permeation chromatography for molecular weight determination was carried out on a TOSOH HLC-8120 GPC system equipped with polystyrene gel columns (TSK GELS, GMH_{HR}-M and GMH_{HR}-L) at 40 °C in *N,N*-dimethylformamide (containing 0.01 mol/L of lithium bromide) at a flow rate of 1.0 mL/min.

Calculations. All the calculations were performed using the program Gaussian-98 on a Compaq Alpha server GS 320. The 6-311G(*d*) basis set was used for geometry optimizations and the 6-311+G(*d,p*) basis set was used for calculation of transition energies and oscillator strengths at the time-dependent density functional theory (TD-DFT) level using the three-parameter Becke-style hybrid functional (B3LYP). Each calculated transition was replaced by a Gaussian broadening function with a width of 0.35 eV to reproduce the shapes of experimental spectra. For aromatic compounds, Gaussian functions with a width of 0.2 eV were used. The calculated absorbance was represented by the oscillator strengths divided by the van der Waals volumes of molecules. The van der Waals volumes were calculated from the optimized geometries using the Slonimski's method,³⁶ in which the van der Waals radii of atoms reported by Bondi³⁷ were used. The calculated values of absorbance cannot be quantitatively compared with the experimental values because calculated oscillator strengths are given in arbitrary units.

Results and Discussion

The basic requirements for single-layer photoresists are transparency at 157 nm, good plasma etch resistance, high T_g , developability in a conventional aqueous base developer, and fine imaging with favorable development characteristics. Although finding materials with one or two of these characteristics is not difficult, identifying materials with all of the properties is quite challenging. Thus, a new copolymer that is both transparent and alkaline soluble was designed. The copolymer was also expected to have other favorable properties such as adhesion, etch resistance, and so on.

As a new transparent group incorporated in resist polymers, we chose a sulfonyl group, which is a strong electron-withdrawing group like a trifluoromethyl group, and can be converted to a wide variety of derivatives such as sulfonates and sulfonamides. Figure 1A shows the calculated VUV spectrum of methanesulfonyl fluoride. The result indicates that a sulfonyl fluoride group should exhibit high transparency at 157 nm. Thus, we became interested in poly(VSF). VSF was prepared easily from sodium isethionate in three steps (Scheme 1).^{38–40} The polymerization of VSF was carried out in a free radical polymerization initiated with AIBN at 40 °C, giving the poly(VSF) as white powder (M_n = 6100, M_w/M_n = 1.15, yield 53%) (Scheme 2). A film was prepared by spin-casting a propylene glycol methyl ether acetate (PGMEA) solution of poly(VSF) on a silicon wafer primed with 1,1,1,3,3-hexamethyldisilazane. The transmittance of the resulting poly(VSF) film was measured with a VUV spectrophotometer and it was found that poly(VSF) film was quite transparent at 157 nm (OD = 2.1 μ m^{−1}). The spectral shape and absorption

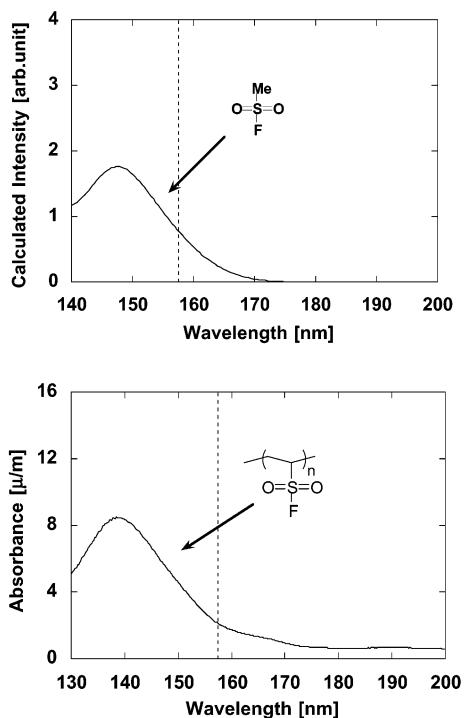
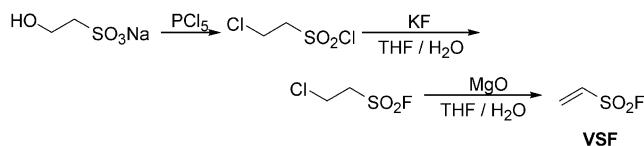
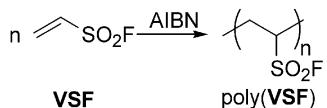


Figure 1. (A) Calculated VUV spectrum of methanesulfonyl chloride. (B) Observed VUV spectrum of poly(VSF).

Scheme 1



Scheme 2



edge are well reproduced in the calculated spectrum (Figure 1B). Noteworthy was that poly(VSF) films showed good adhesion to silicon wafers, which is contrary to most transparent polymers bearing the fluorine hydrophobic character. A carbonyl ester group that gives good solubility and adhesion to polymers has been proved to show substantial absorption in the VUV region due to the $\pi-\pi^*$ transitions. Thus, a C=O moiety is not generally suitable for the design of 157-nm photoresist platforms.^{33,41} However, the ester functionality in close proximity of CF₃ has been shown to be quite transparent and useful in the design of 157-nm resist polymers.^{4,5} VSF with a polar functional group can be used as a substitute to C=O group, and should give other essential properties to photoresist platforms.

In addition to the high transparency at the exposure wavelength and an adequate adhesion, plasma etching resistance and development in aqueous base solution are required for single-layer photoresists. Taking these requirements into consideration, we chose HFIST as a comonomer. Hexafluoro-2-propanol has been reported to have high transparency at 157 nm and also has a *pKa* value of around 10 due to the two electron-withdrawing CF₃ groups adjacent to the hydroxyl group, which is comparable to phenols.⁴² This group has been

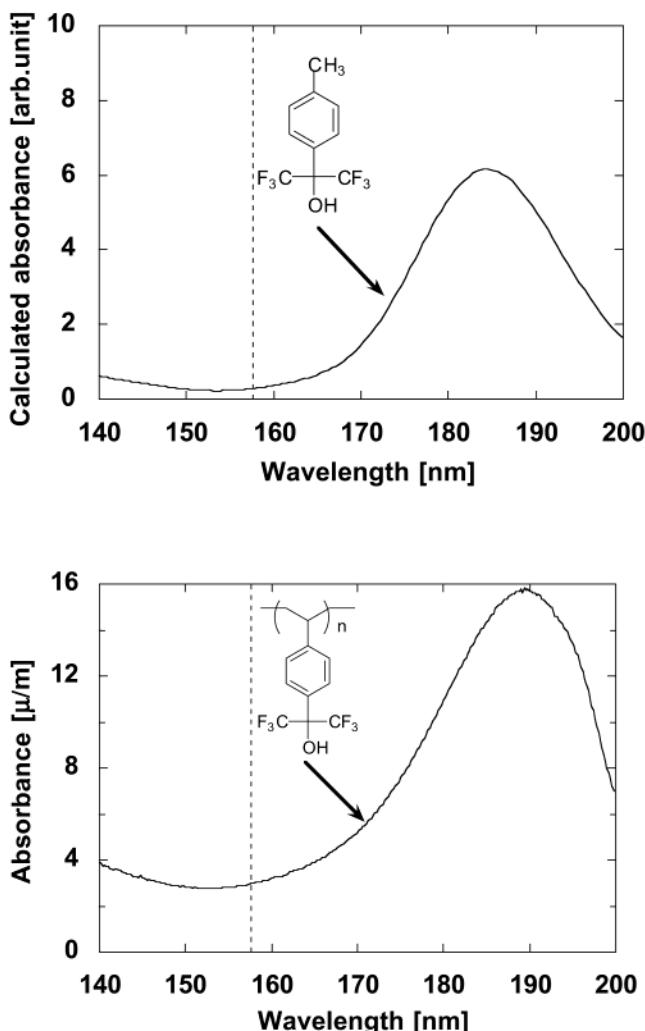


Figure 2. (A) Calculated VUV spectrum of 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)toluene. (B) Observed VUV spectrum of poly(HFIST).

attached directly to polystyrene to produce a base-soluble polymer for 248-nm lithography.⁴³ Our calculation method was also applied to estimation of the spectrum of HFIST. The calculated spectrum of HFIST, where 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)toluene was used as a model compound, indicates this repeat unit should be transparent enough at 157 nm (Figure 2A). The VUV spectrum of poly(HFIST) obtained by a free radical polymerization of HFIST coincides well with the shape of the calculated spectrum and indicates adequate transparency at 157 nm (OD = 3.0 μm^{-1}) (Figure 2B).

On the basis of the initial findings, a copolymer of VSF and HFIST was chosen as a candidate for a 157-nm photoresist platform. A free radical copolymerization of equimolar amounts of VSF with HFIST was performed in bulk at 75 °C using AIBN as an initiator, giving poly(VSF-*co*-HFIST) with a high molecular weight ($M_n = 150\,000$, $M_w/M_n = 2.6$, yield 75%) (Scheme 3). The IR spectrum of poly(VSF-*co*-HFIST) exhibited characteristic SO₂F and CF₃ bands at 1403 and 1218 cm^{-1} , respec-

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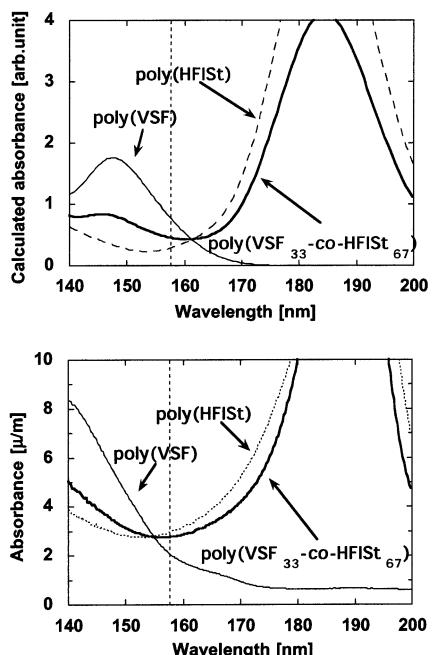
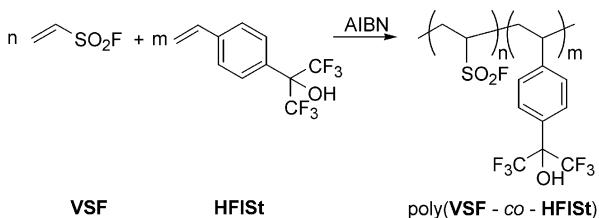


Figure 3. (A) Calculated VUV spectra of poly(VSF₃₃-co-HFIST₆₇), poly(VSF), and poly(HFIST). (B) Observed VUV spectra of poly(VSF₃₃-co-HFIST₆₇), poly(VSF), and poly(HFIST).

Scheme 3



tively, which indicates that both VSF and HFIST monomers were introduced into the poly(VSF-*co*-HFIST). In addition, the molar ratio of VSF and HFIST in the copolymer was determined to be 1:2 by sulfur analysis.

TG and DSC of poly(VSF₃₃-*co*-HFIST₆₇) indicated that no thermal decomposition occurred up to 300 °C and the glass transition was observed at 142 °C.

The calculated VUV spectra of poly(VSF₃₃-*co*-HFIST₆₇), poly(VSF), and poly(HFIST) are shown in Figure 3A, which were obtained by adding the calculated spectra of VSF and HFIST in proportion to the copolymer composition. The calculated spectra agree well with the observed spectra (Figure 3B), and the OD value of poly(VSF₃₃-*co*-HFIST₆₇) was determined as 2.8 μm⁻¹ at 157 nm.

Another requirement for photoresists is acid-catalyzed solubility switching property. Although C=O bond generally shows a strong absorption around 157 nm region, *tert*-butoxycarbonyl (*tert*-BOC)-protected poly(HFIST) has been reported to have a relatively low absorbance (OD = 3.5 μm⁻¹).²⁴ To confirm this finding, samples of *tert*-BOC-protected poly(HFIST) in various protecting ratios were synthesized. Partial protections were successfully carried out by reacting poly(HFIST) with di-*tert*-butyl dicarbonate in the presence of DMAP as a base catalyst. The exact protecting ratios were calculated from the weight loss values measured by TG analysis. Poly(HFIST)s protected with 40, 55, 70, and 100% *tert*-BOC were synthesized. The VUV measure-

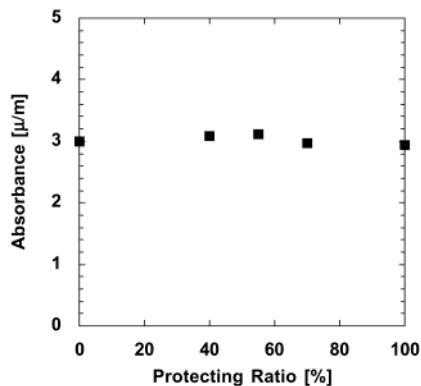


Figure 4. Absorbances at 157 nm for various *tert*-BOC-protected poly(HFIST)s.

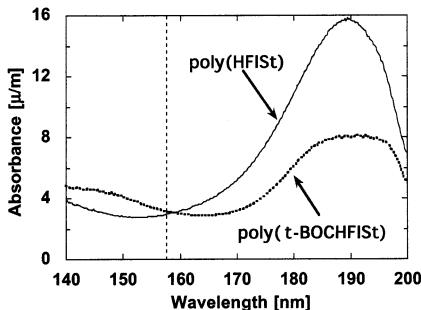


Figure 5. VUV spectra of poly(HFIST) and 100% *tert*-BOC-protected poly(HFIST).

ments of these polymers supported the reported results and no critical increase on their absorbances was observed (Figure 4). This behavior is clarified by comparing the VUV spectrum of 100% *tert*-BOC-protected poly(HFIST) with that of poly(HFIST) without protection (Figure 5). As shown in the figure, incorporation of the *tert*-BOC group effectively reduces the peak height at 189 nm which is assigned to the π-π* transition at the aromatic ring. Thus, we introduced the *tert*-BOC group in the base-soluble hexafluoro-2-propanol as a protecting group. Copolymers with various protecting ratios (30, 45, 70, 93 wt %) were synthesized in order to determine the appropriate protecting ratios, which should give the polymer a favorable dissolution property and adequate transparency as well. The VUV measurement of these polymers indicated the *tert*-BOC group could be incorporated in high amounts to obtain a dissolution contrast while still maintaining a reasonable transparency at 157 nm.

Considering the resist line-edge roughness and alkaline dissolution rate of the copolymers, the molecular weight of the copolymers should be decreased to around $M_n = 10\,000$.⁴⁴ Efforts to reduce the molecular weight were successfully performed by solution polymerization using toluene as a solvent. Copolymerization of equimolar amounts of VSF with HFIST at 0.25 mol/L was performed at 60 °C for 50 h, giving relatively low molecular weight polymer ($M_n = 13\,000$) in 5% yield as shown in Table 1. Although the dilution method rendered the molecular weight lower, the VSF content introduced to the copolymer and yield were decreased. From the elemental analysis, the molar ratio of VSF and HFIST in the copolymer was determined to be 1:3. Thus,

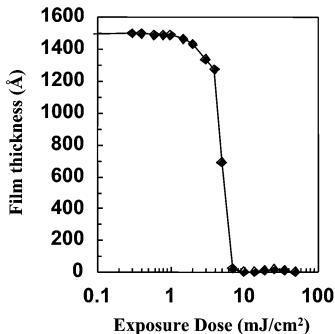
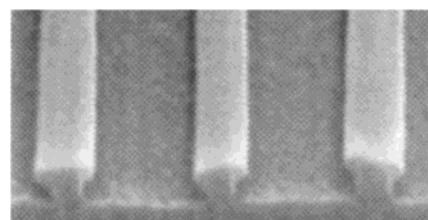
Table 1. Synthesis of Poly(VSF)-*co*-poly(HFIST)^a

run	[M] ₀ ^b	[VSF] ₀ ^c [HFIST] ₀	yield ^d (%)	<i>M</i> _n ^e	<i>M</i> _w / <i>M</i> _n ^e	<i>T</i> _g ^f (°C)	unit ratio ^g
1	1	1:1	46	30 000	1.5	137	26:74
2	0.25	1:1	5	13 000	1.4	128	24:76
3	1	5:1	17	17 000	1.5	136	40:60
4	0.5	5:1	9	14 000	1.3	132	39:61

^a Polymerization was conducted with 1 mol % AIBN in toluene at 60 °C for 50 h. ^b Initial monomer concentration. ^c Monomer feed ratio. ^d Isolated yield after precipitation with hexane. ^e Determined by GPC (PSt, DMF). ^f Determined by DSC at a rate of 5 °C/min under N₂. ^g Unit ratio of VSF and HFIST components in polymer determined by elemental analysis.

decreasing the amounts of VSF unit might damage the transparency of the copolymer. This problem was solved by changing the monomer feed ratio of VSF/HFIST from 1:1 to 5:1. This method worked well with increasing VSF unit into the copolymer. Polymerization was performed at a 1 mol/L monomer concentration at 60 °C for 50 h, producing poly(VSF-*co*-HFIST) (the molar ratio of VSF and HFIST units = 2:3) with the *M*_n = 17 000 and *M*_w/*M*_n = 1.5. *T*_{gs} of the copolymers were around 135 °C, and their thermal decomposition temperatures were maintained up to 300 °C. Furthermore, the OD of poly(VSF₄₀-*co*-HFIST₆₀) was improved to 2.4 μm⁻¹.

On the basis of the findings above, poly(VSF₄₀-*co*-HFIST₂₂-*co*-*tert*-BOC HFIST₃₈) (OD = 2.8 μm⁻¹) was prepared from poly(VSF₄₀-*co*-HFIST₆₀) and di-*tert*-butyl dicarbonate in the presence of DMAP. A preliminary formulation was made by dissolving poly(VSF₄₀-*co*-HFIST₂₂-*co*-*tert*-BOC HFIST₃₈) and 5 wt % triphenylsulfonium trifluoromethanesulfonate (triflate) as a PAG in PGMEA. The resist film had an OD value of 3.1 μm⁻¹. Lithography characteristics were studied using a F₂ laser exposure system (Vuves-4500, LithoTech Japan). The sensitivity curve as shown in Figure 6 indicates that the sensitivity and contrast are 7.2 mJ cm⁻² and 3.1, respectively, when a 150-nm-thick resist film prebaked at 100 °C for 1 min was exposed to a 157-nm laser and postbaked at 130 °C for 1 min. This was followed by developing with a 2.38 wt % TMAH aqueous solution. Figure 7 shows the cross-sectional scanning electron micrograph (SEM) image of 120-nm line pattern obtained by contact exposure. Although the pattern profile was T-top shaped due to the uncontrolled amine concentration in the exposure atmosphere, the vertical side wall was obtained. This result indicates the partially *tert*-BOC-protected poly(VSF-*co*-HFIST) would work as a high-sensitive and high-contrast resist platform.

**Figure 6.** Exposure characteristic curve for the system of poly(VSF₃₃-*co*-HIFSt₂₂-*co*-*tert*-BOC HFIST₃₈) and 5 wt % triphenylsulfonium triflate.

Conclusions

Our molecular orbital calculations of the photoabsorption of molecules in the VUV region predicted that a sulfonyl fluoride group should exhibit excellent transparency in this region. The experimental measurement of poly(VSF) clearly supported this result and showed a significantly low OD of 2.1 μm⁻¹. Novel copolymer from VSF and HFIST was prepared by a free radical copolymerization, in which the VSF unit was responsible for the transparency of the copolymer and the HFIST unit was responsible for the alkaline solubility. It has been found that this copolymer is transparent at 157 nm and the OD of poly(VSF₄₀-*co*-HFIST₆₀) was determined to be 2.4 μm⁻¹. The resist system based on the partially *tert*-BOC-protected poly(VSF-*co*-HFIST) and triphenylsulfonium triflate showed low absorbance and excellent sensitivity as the 157 nm resist.