A New Photoresist Material for 157 nm Lithography-2

T. Fujigaya*1, S. Ando*1, Y. Shibasaki*1, S. Kishimura*2, M. Endo*2, M, Sasago*2, M. Ueda*1.

*1 Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 0-okayama 2-12-1, Meguro, Tokyo 152-8552, Japan mueda@polymer.titech.ac.jp
*2 ULSI Process Technology Development Center, Semiconductor Company, Matsushita Electric Industrial Co., Ltd., 19, Nishikyo-Kasuga-cho, Minami-ku, Kyoto 601-8413, Japan

Time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional suggested that sulfonic acid esters are transparent at around 157 nm region. Based on these findings, poly(methyl vinyl sulfonate) [poly(VSO3Me)] was prepared and found to have an extremely low absorbance (Abs.) of 2.2 µm⁻¹ at 157 nm. Various alkyl vinyl sulfonates (VSO3R)s were prepared from 2-chloroethanesulfonyl chloride and alcohol components in the presence of pyridine, and their radical polymerizations were conducted in bulk using 2,2'-azobisisobutyronitrile as an initiator. Polymerizations of primary and secondary VSO3Rs bearing small alkyl substituents gave homopolymers with high molecular weights. Among them, the Abs. of poly(2,2,2-trifluoroethyl vinyl sulfonate) reached to 1.3 µm⁻¹. Various copolymers from alkyl vinyl sulfonates and 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene (HFISt) were also prepared and the Abs. of poly(1,1,1,3,3,3-hexafluoroisopropyl vinyl sulfonate-co-HFISt₉₀) [poly(VSO3iPr₆F₄₀-co-HFISt₆₀)] was found to be 2.4 µm⁻¹ at 157 nm. The photoresist consisting of partially t-BOC-protected poly(VSO3iPr₆F₄₀-co-HFISt₂₈-co-t-BOCHFISt₃₂) (Abs. 2.6) and an photoacid generator showed the contrast and sensitivity of 10.3 and 5.0 mJ cm⁻², respectively. 

Keywords: 157 nm lithography, poly(alkyl vinyl sulfonate)s, photoacid generator, chemically amplified photoresist

1. Introduction

In a preceding paper [1], we have reported a new approach for the design of a novel 157 nm resist platform having most of the properties required for a single layer photoresist, such as transparency, high glass transition temperature (Tₐ), solubility, adhesion, and so on. We have also demonstrated that time-dependent density functional theory (TD-DFT) calculations using the B3LYT hybrid functional played a great important role in the designing such resist materials [2]. Our calculation method nicely reproduces the experimental spectra of molecules in the vacuum ultraviolet (VUV) region and can predict the transparency of various polymeric materials in high precision. With a help of this method, we found that poly(vinyl sulfonyl fluoride) [poly(VSF)] possess a high transparency in the VUV region, and in facts, poly(VSF) showed a significantly low absorbance (Abs.) of 2.1 µm⁻¹ [1]. Based on these findings, a new 157 nm resist platform of poly[vinyl sulfonyl fluoride-co-4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene] [poly(VSF₄₀-co-HFISt₆₀)] was developed. These results encouraged us to investigate not only poly(VSF) but also poly(alkyl vinyl sulfonate)s (poly(VSO3R)s as a novel photoresist platform.

In this paper, we employed the combination of the TD-DFT calculations and experimental measurements of VUV spectra for polymers again. From these approaches, we found that
poly(VSO3R)s possess high transparency. Then, various VSO3Rs were synthesized and copolymerized with HFISt to evaluate the transparency and thermal stability. Although aromatic systems are generally inferior in their transparency to aliphatic ones, they are superior in etch resistance. Furthermore, it is noted that incorporation of aromatic rings in copolymers proved to be beneficial to stabilize the photo-induced free radicals and tend to induce radical termination than fragmentation. As a result, the amount of outgassing, which is one of the critical problems to overcome in the 157 nm resists, could be reduced [3].

2. Experimental

2.1. Materials

4-Chlorostyrene was distilled from CaH2. Tetrahydrofuran (THF) was dried over sodium and distilled twice prior to use. Dichloromethane (CH2C12) was distilled from CaH2. 2,2’-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Triphenylsulfonylimide was supplied by Midori Kagaku Co. Propylene glycol monomethyl ether acetate (PGMEA) and an aqueous 2.38 wt % tetramethylammonium hydroxide (TMAH) solution was used as a casting solvent and an aqueous base developer, respectively. Column chromatography: silica gel 60 (Merck 0.063-0.200 mm). Methanol, butanol, and isopropanol were distilled from CaO and successive distillation from Mg was done before use. 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-hexafluoropropanol were distilled from CaSO4 and 3A molecular sieves, respectively. Cyclohexanemethanol and cyclohexanol were distilled from CaO. Other reagents were purchased and used as received.

Caution!

2-Chloroethanesulfonyl chloride, 2,2,2-trifluoroethyl vinyl sulfonate, and 1,1,1,3,3,3-hexafluoropropanoyl vinyl sulfonate are severe eye and skin irritants. 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.


Powdered phosphorus pentachloride (400 g, 1.92 mol) and sodium isethionate (118 g, 0.8 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 the ice-water until unreacted phosphoryl chloride had completely reacted with water. The oil was separated, taken up in toluene, and dried over calcium chloride. After removing the organic layer with a rotary evaporator, the residue was distilled to give 2-chloroethanesulfonyl chloride as a colorless oil. Yield; 120 g, (92 %, 80-81 °C / 10 mmHg. lit; 77-79 °C / 4 mmHg. 61 % [4]). IR (KBr): v 2992, 2935 (-CH2), 1376 (-SO2Cl). 1H-NMR (300 MHz CDCl3): δ 3.97-4.10 (m, 4H, -CH2-). 13C-NMR (75 MHz CDCl3): δ 35.9, 66.2. Anal. calc. for C9H14O3S; C 14.73, H 6.47, S 19.67. Found: C 14.37, H 2.50, S 19.29.

2.3. Synthesis of VSO3Rs: General procedure

To a solution of 2-chloroethanesulfonyl chloride (10 mmol) dissolved in CH2Cl2 (20 mL), an alcohol (1.2 equiv) was added, and the solution was cooled with an ice-bath. Pyridine (2.2 equiv) was added to the well-cooled stirred reaction solution through a dropping funnel under N2 flow. The mixture was stirred for 1.5 h at room temperature. As for VSO3Me, VSO3CF3Et, VSO3iPr6F, the mixture was worked up by washing with a cold 10 % aqueous Na2CO3 (50 mL twice) solution, water (50 mL), 1M HC1 aqueous solution (50 mL twice) and water (50 mL). And as for the other VSO3Rs, the mixture was worked up by washing with 1 mol/L HCl aqueous solution (50 mL twice) and water (50 mL). The organic layer was dried over magnesium sulfate and the solvents were removed with a rotary evaporator to yield the products. The products were purified as follows.

Methyl vinyl sulfonate (VSO3Me)

Purified by vacuum distillation. Colorless oil. Yield; 0.50 g (41 %; 64-66 °C / 4 mmHg). IR (KBr): v 3.84 (s, 3H, -CH3), 6.18 (d, 1H, CH2Hb=, J=9.0 Hz, J=75.5 Hz), 6.53 (dd, 1H, CH2Hb=, J=16.5 Hz, J=75.5 Hz), 6.53 (dd, 1H, =CHa, J=16.5 Hz, J=9.0 Hz). 13C-NMR (75 MHz CDCl3): δ 56.9, 131.4, 132.2. Anal. calc. for C3H6O3S; C 29.50, H 4.95, S 26.25. Found; C 29.11, H 4.97, S 26.22.

Cyclohexylmethyl vinyl sulfonate (VSO3CyMe)

Purified by column chromatography (CH2Cl2
was used as an eluent). White powder. Yield; 0.61 g (30 %). IR (KBr): ν 2927 (-CH₂-), 1361 (-SO₂-), 1172, 971, 948, 833. ¹H-NMR (300 MHz CDCl₃): δ 0.92-1.05 (m, 2H, -CH₂-), 3.91 (d, 2H, -CH₂-, J=6.0 Hz), 6.13 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=90.3 Hz), 6.39 (d, 1H, CH=Hₓ, Jₓ=90.3 Hz), 6.58 (dd, 1H, 1H, CH=Hₓ, Jₓ=16.9 Hz, Jₓ=90.3 Hz). IR (KBr): ν 2937 (-CH₂-), 1357 (-SO₂-), 1172, 933, 910, 867. 'H-NMR (300 MHz CDCl₃): δ 0.92-1.05 (m, 2H, -CH₂-), 1.14-1.33 (m, 3H, -CH₃, -CH₂-), 3.91 (d, 2H, -CH₂-, J=6.0 Hz), 6.13 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=90.3 Hz), 6.39 (d, 1H, CH=Hₓ, Jₓ=90.3 Hz), 6.58 (dd, 1H, 1H, CH=Hₓ, Jₓ=16.9 Hz, Jₓ=90.3 Hz). IR (KBr): ν 2938 (-CH₂-), 1357 (-SO₂-), 1172, 933, 910, 867. 'H-NMR (300 MHz CDCl₃): δ 0.92-1.05 (m, 2H, -CH₂-), 1.14-1.33 (m, 3H, -CH₃, -CH₂-), 3.91 (d, 2H, -CH₂-, J=6.0 Hz), 6.13 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=90.3 Hz), 6.39 (d, 1H, CH=Hₓ, Jₓ=90.3 Hz), 6.58 (dd, 1H, 1H, CH=Hₓ, Jₓ=16.9 Hz, Jₓ=90.3 Hz). ¹C-NMR (75 MHz CDCl₃): δ 23.5, 78.2, 129.6, 134.2. Anal. calc. for C₉H₁₆O₃S: C 52.91, H 7.89, S 15.70. Found: C 52.80, H 7.92, S 15.69.

Cyclohexyl vinyl sulfonate (VSO₃Cy)

Purified by column chromatography (CH₂Cl₂ was used as eluent). Colorless oil. Yield; 0.86 g (45 %). IR (KBr): ν 2938 (-CH₂-), 1357 (-SO₂-), 1172, 933, 910, 867. ¹H-NMR (300 MHz CDCl₃): δ 1.26-1.97 (m, 10H, -CH₂-), 4.55 (m, 1H, -CH₃), 6.09 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=77.7 Hz), 6.39 (d, 1H, CH=Hₓ, Jₓ=16.5 Hz, Jₓ=90.3 Hz), 6.54 (dd, 1H, 1H, CH=Hₓ, Jₓ=16.5 Hz, Jₓ=9.6 Hz). ¹C-NMR (75 MHz CDCl₃): δ 25.9, 26.6, 29.6, 37.7, 76.2, 130.5, 132.9. Anal. calc. for C₈H₁₄O₃S: C 50.50, H 7.42, S 16.85. Found: C 50.30, H 7.42, S 16.82.

Butyl vinyl sulfonate (VSO₃Bu)

Purified by vacuum distillation. Colorless oil. Yield; 0.49 g (30 %; 62-64 °C 13 mmHg). IR (KBr): ν 1357 (-SO₂-), 1172, 1099, 917, 790. 'H-NMR (300 MHz CDCl₃): δ 0.94 (tr, 3H, CH₃, J₆=7.8 Hz), 1.42 (m, 2H, -CH₂-), 1.71 (m, 2H, -CH₂-), 4.13 (tr, 2H, -O-CH₂-, J₆=6.3 Hz), 6.14 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=81.8 Hz), 6.41 (d, 1H, CH=Hₓ, Jₓ=16.5 Hz, Jₓ=99.1 Hz), 6.56 (dd, 1H, 1H, =CHₓ, Jₓ=16.5 Hz, Jₓ=9.6 Hz). ¹C-NMR (75 MHz CDCl₃): δ 14.0, 19.2, 31.4, 71.3, 130.6, 133.0. Anal. calc. for C₆H₁₂O₃S: C 43.88, H 7.37, S 19.53. Found: C 44.07, H 7.26, S 19.62.

Isopropyl vinyl sulfonate (VSO₃iPr)

Purified by vacuum distillation. Colorless oil. Yield; 0.83 g (55 %; 78-79 °C / 3 mmHg). IR (KBr): ν 1376 (-SO₂-), 1172, 910, 875. ¹H-NMR (300 MHz CDCl₃): δ 1.40 (d, 6H, CH₃, J₆=6.0 Hz), 4.82 (m, 1H, CH=, J=6.0 Hz), 6.08 (d, 1H, CH=Hₓ, Jₓ=9.6 Hz, Jₓ=91.9 Hz), 6.39 (d, 1H, CH=Hₓ, Jₓ=91.9 Hz), 6.56 (dd, 1H, 1H, =CHₓ, Jₓ=16.5 Hz, Jₓ=9.6 Hz). ¹C-NMR (75 MHz CDCl₃): δ 22.9, 29.1, 29.9, 30.2 33.8, 34.1, 35.6, 36.6, 37.1, 38.5, 38.7, 39.4, 40.1, 41.6, 73.3, 74.2, 130.6, 132.9. Anal. calc. for C₅H₁₀O₃S: C 55.83, H 7.40, S 14.82. Found: C 55.53, H 7.46, S 14.82.

2-endo-Norbornyl vinyl sulfonate (VSO₃endo-NB)

Purified by column chromatography (CH₂Cl₂ was used as an eluent). Colorless oil. Yield; 0.9 g (42 %). Mixture of endo and exo compounds. IR (KBr): ν 2954 (-CH₂-), 2869 (-CH₂-), 1361 (-SO₂-), 1172, 1099, 948, 848, 825. ¹H-NMR (300 MHz CDCl₃): δ 1.20-1.92 (m, 5H, 1H, -CH₂-, J=6.0 Hz), 6.12-6.60 (m, 3H, CH=Hₓ=CHₓ). ¹C-NMR (75 MHz CDCl₃): δ 23.5, 78.2, 129.6, 134.2. Anal. calc. for C₅H₁₀O₃S: C 39.98, H 6.71, S 21.35. Found: C 39.56, H 6.78, S 20.93.
1.85-2.06 (m, 2H, -CH2-, -CH<), 2.25 (m, 1H, -CH2-), 2.53 (m, 1H, -CH2-), 4.81-4.89 (m, 1H, -CH<) , 6.14 (d, 1H, CH_b=, J=9.6 Hz, Jbc=80.7 Hz), 6.47 (d, 1H, CH_Hb=, Jab=16.7 Hz, Jbc=80.7 Hz), 6.55 (dd, 1H, =CHa, Jab=16.7 Hz, Jac=9.6 Hz). 13C-NMR (75 MHz CDC13): δ 21.2, 29.7, 36.8, 37.4, 37.6, 41.8, 84.0, 129.8, 134.0. Anal. calc. for C9H14O3S; C 53.44, H 6.98, S 15.85. Found: C 53.53, H 6.88, S 15.42.

1-Adamantylmethyl vinyl sulfonate (VSO3AdMe)

Purified by column chromatography (CH2Cl2 was used as an eluent). White powder. Yield; 1.0 g (39 %; mp = 46 °C). IR (KBr): ν 2904 (-CH2-), 1361 (-502-), 1172, 960, 848. 1H-NMR (300 MHz CDC13): δ 1.55 (s, 3H, -CH2-), 1.56 (s, 3H, -CH2-), 1.65-1.72 (m, 6H, -CH<, -CH2-), 2.00 (s, 3H, -CH2-), 3.67 (s, 2H, -CH2-), 6.12 (d, 1H, CH~Hb=, Jac=9.6 Hz, Jbc=80.7 Hz), 6.39 (d, 1H, CH J =, Jab=16.7 Hz, Jbc=80.7 Hz), 6.53 (dd, 1H, =CHa, Jab=16.7 Hz, Jac=9.6 Hz). 13C-NMR (75 MHz CDC13): 8 28.4, 34.0, 37.2, 39.3, 80.6, 130.5, 132.9. Anal. calc. for C13H2u035; C 60.91, H 7.86, S 12.51. Found: C 61.10, H 7.96, S 12.65.

2-Adamantyl vinyl sulfonate (VSO3Ad)

Purified by column chromatography (CH2Cl2 was used as an eluent). White powder. Yield; 1.0 g (41 %; mp = 32 °C). IR (KBr): ν 2908 (-CH2-), 1357 (-SO2-), 1172, 933, 867. 1H-NMR (300 MHz CDC13): δ 1.57-1.61 (m, 2H, -CH2-), 1.74 (m, 4H, -CH2-, -CH<), 1.83-1.92 (m, 4H, -CH2-, -CH<), 2.07-2.15 (m, 4H, -CH2-, -CH<), 6.07 (d, 1H, CH_b=, J=9.9 Hz, Jbc=97.8 Hz), 6.40 (d, 1H, CH_Hb=, Jab=16.7 Hz, Jbc=97.8 Hz), 6.59 (dd, 1H, =CHa, Jab=16.7 Hz, Jac=9.9 Hz). 13C-NMR (75 MHz CDC13): δ 27.0, 27.3, 31.5, 33.3, 36.8, 37.5, 87.2, 129.2, 134.3. Anal. calc. for C12H18035; C 59.47, H 7.49, S 13.23. Found: C 58.89, H 7.38, S 12.65.

2-Hydroxy-3-pinanyl vinyl sulfonate (VSO3Pina)

Purified by column chromatography (CH2Cl2 was used as an eluent). White powder. Yield; 1.3 g (50 %; mp = 36 °C). IR (KBr): ν 3536 (-OH), 3421 (-OH), 2915 (-CH2-), 1357 (-SO2-), 983, 879. 1H-NMR (300 MHz CDC13): δ 0.97 (s, 3H, -CH3), 1.29 (s, 3H, -CH3), 1.38 (d, 3H, -CH3, J =1.2 Hz), 1.56 (d, 1H, -CH<, J =9.9 Hz), 1.93-1.99 (m, 2H, -CH2-), 2.43 (tr, 1H, -CH2-, J =5.7 Hz), 2.22-2.30 (m, 1H, -CH2-), 2.35 (s, 1H, -OH), 2.46-2.56 (m, 1H, -CH2-), 4.91 (q, 1H, CH, J =9.9 Hz, J =5.7 Hz), 6.16 (d, 1H, CH_b=, J=9.6 Hz, Jbc=93.9 Hz), 6.47 (d, 1H, CH_Hb=, Jab=16.8 Hz, Jbc=93.9 Hz), 6.66 (dd, 1H, =CHb, Jab=16.8 Hz, Jac=9.6 Hz). 13C-NMR (75 MHz CDC13): δ 24.9, 28.3, 28.9, 29.9, 36.0, 39.1, 41.0, 54.6, 74.2, 80.9, 130.5, 134.0. Anal. calc. for C12H2o04S; C 55.36, H 7.74, S 12.32. Found: C 55.72, H 7.54, S 12.23.

2.4.

4-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropyl)styrene (HFIS) [5]

A 500 ml three neck flask equipped with a condenser and a three-way stopcock connected to vacuum pump was evacuated and dried carefully with a heat gun, then flushed with nitrogen. Magnesium (8.0 g, 0.33 mol) was placed and activated in vacuo with vigorous stirring for a few hours. The system was maintained at 45 °C under nitrogen. THF (2 mL) and dibromomethane (0.1 mL) were added. After the activation of magnesium, a solution of 4-chlorostyrene (40 g, 0.29 mol) dissolved in THF (250 mL) was added dropwise to the reaction flask at such a rate to maintain a gentle reflux. The reaction was refluxed for 1 h after all 4-chlorostyrene had been added. After the reaction was completed, the reaction solution was poured into a new three neck flask equipped with a cold-finger condenser, a three-way stopcock, and a rubber cap, which was dried with a heat gun and purged with nitrogen previously. Then, the rubber cap was replaced with a gas inlet tube connected to a 500 mL of two-neck flask equipped with dropping funnel. Trihydrous hexafluoroacetone (75 g, 0.34 mol) was added dropwise to sulfuric acid (300 mL) heated at 140 °C and anhydrous hexafluoroacetone gas produced was introduced to a 4-vinylphenyl magnesium chloride solution at 0 °C. After addition of anhydrous hexafluoroacetone gas, the mixture was allowed to warm to room temperature and stirred for 2 h. The color of mixture became to dark brown. To this solution, 6 mol/L HCl aqueous solution was added slowly until the solution was separated to clear 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 with a rotary evaporator. The residue was purified by vacuum distillation and successive gradient column chromatography (hexane to dichloromethane) to give
4-(1,1,1-trifluoro-2-hydroxypropyl)styrene as a colorless liquid. Yield: 64.0 g (74 %, 40-45 °C / 1 mmHg). IR (KBr): ν (-OH), 1211 (-CF3).
1H-NMR (300 MHz CDC13): 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).
13C-NMR (75 MHz CDC13): δ 116.4, 123.2 (J=285.7 Hz), 126.9, 127.3, 129.1, 136.3, 140.1.
Anal. calc. for C11H8F6O: C 48.90, H 2.98, F 42.19; Found: C 48.06, H 3.05, F 42.13.

2.5. Homopolymerizations of VSO3R; Typical procedure
VSO3Me (0.24 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 the specified temperature for 24 h. Then, the tube was opened and the polymer was purified by precipitation from acetone into hexane three times and water once. After purification, the polymer was dried in vacuum. The polymer was obtained as a white powder.

2.6. Copolymerization of VSO3R with HFtSt; Typical procedure
VSO3Me (0.24 g, 2 mmol), HFtSt (0.56 g, 2 mmol) and AIBN (6.5 mg, 0.04 mmol) were charged into a polymerization tube followed by several cycles of freeze and thaw. The tube was sealed and heated at the specified temperature for 24 h. Then, the tube was opened and the polymer was purified by precipitation from acetone into hexane three times and water once. After purification, the polymer was dried in vacuum. The polymer was obtained as a white powder.

2.7. Lithographic Evaluation
Resist films were prepared by casting a solution in propylene glycol monomethyl ether acetate (PGMEA) on silicone wafers. Pre-bake was performed at 90–100 °C for 60 sec. All resists used triphenylsulfonium triflate as a photoacid generator at an approx. 3–5 wt%. Post exposure bake (PEB) was performed at 120–150°C for 60 sec. The 157 nm exposure was carried out with a F2 laser exposure system VUVES-4500 (Litho Tech Japan). VUV spectra were measured on a VUV-200 (JASCO).

2.8 Measurements
FT-IR spectra were measured with a Horiba FT-720 spectrophotometer. 1H and 13C NMR spectra were recorded with a BRUKER DPX-300 spectrometer. Number- and weight average molecular weights were determined by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8120GPC system equipped with two polystyrene gel columns (TSK gels GMHHR-M and GMHHR-L) using N,N-dimethylformamide (DMF, 5.8 mmol/L lithium bromide solution) as an eluent at a flow rate of 1.0 mL/min, polystyrene calibration, and reflective index (RI) detector. Thermal analyses were performed with a Seiko SSS5000 TG-DTA 220 thermal analyzer at a heating rate of 10 °C min-1 for thermogravimetric analysis (TGA) and a Seiko SSS5000 DSC220 at a heating rate of 5 °C min-1 for differential scanning calorimetry (DSC) under a nitrogen atmosphere, respectively. The Abs. of resist films on MgF2 substrate were measured with a F2 laser exposure system VUVES-4500 (Litho Tech Japan). VUV spectra were measured on a VUV-200 (JASCO).

3. Results and Discussion
3.1. Determination of high transparent polymer at 157 nm
To investigate the transparency of sulfonic acid esters, the VUV spectrum of methyl methanesulfonate was calculated as a representative sulfonic acid ester by using time-dependent density functional theory (TD-DFT) calculations. However, it showed a broad absorption peak at around 157 nm region (Figure 1 a).

[Figure 1a. Calculated VUV spectrum of methyl methanesulfonate]

To make sure of this result, poly(methyl vinyl sulfonate) [poly(VSO3Me)] was synthesized by free radical polymerization using AIBN as an initiator. Figure 1b shows the VUV spectrum of poly(VSO3Me). No absorption peak
was observed at around 157 nm and its Abs. was determined to be 2.2 µm⁻¹. The discrepancy between the calculation and experiment would be attributable to the structure of model compound. When methyl ethanesulfonate was employed as a model, the calculated spectrum agreed well with the experimental spectrum of poly(VSO3Me) (Figure 2).

![Figure 1b. VUV spectrum of poly(VSO3Me)](image1)

![Figure 2. Calculated VUV spectrum of methyl ethanesulfonate](image2)

![Figure 3a. Calculated VUV spectra of alkyl methanesulfonic acid esters](image3)

![Figure 3b. Calculated VUV spectra of alkyl ethanesulfonic acid esters](image4)

Polar functional groups are essential because these groups give the physical properties required for a single layer photoresist such as solubility for a casting solvent, high Tg, adhesion to various substrates, and so on. As a polar functional group, a carbonyl ester group (RCOOR') has been widely known and employed for these platforms. The RCOOR' group, however, causes substantial absorption in the VUV region due to the π-π* transitions at the C=O moiety [6]. The development of single layer photoresists for 157 nm lithography has been facing a dilemma in this aspect. Meanwhile, we have targeted sulfonic acid esters having high transparency at around 157 nm region as an ideal substitute for carbonyl esters. The calculated spectra indicated that sulfonic acid esters (RSO2OR')s exhibited significantly lower Abs.s than those of the corresponding carboxylic acid esters (RCOOR') [6]. This originates from the absence of π-π* transitions at the -SO2O- moiety. Thus, various polymerizable VSO3Rs were prepared and copolymerized with 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-styrene (HF1St) for the resists formation as described below.

3.2. Preparation of VSO3R

VSO3Rs were obtained by the reaction of corresponding alcohols and 2-chloroethane-
sulfonyl chloride in the presence of pyridine [7] (Scheme 1). As a series of VS03Rs, methyl vinyl sulfonate (VS03Me), butyl vinyl sulfonate (VS03Bu), cyclohexylmethyl vinyl sulfonate (VS03CyMe), norbornenylmethyl vinyl sulfonate (VS03NBMe), 1-adamantylmethyl vinyl sulfonate (VS03AdMe), isopropyl vinyl sulfonate (VS03iPr), cyclohexyl vinyl sulfonate (VS03Cy), 2-endo-norbornyl vinyl sulfonate (VS03-endo-NB), 2-adamantyl vinyl sulfonate (VS03Ad), 2-hydroxy-3-pinanyl vinyl sulfonate (VS03Pina), 2,2,2-trifluoroethyl vinyl sulfonate (VS03CF3Et), and 1,1,1,3,3,3-hexafluoroisopropyl vinyl sulfonate (VS03iPr6F) were synthesized (Table 1).

The efforts to prepare tertiary VS03Rs for example tert-butyl vinyl sulfonate or 1-adamantyl vinyl sulfonate resulted in decomposition of products during purification by column chromatography. These difficulties in preparing tertiary sulfonic acid esters have been reported so far [8]. Attempt to prepare 2-exo-norbornyl vinyl sulfonate also resulted in decomposition. It is widely known that the solvolysis rate of 2-exo-norbornyl sulfonate is unexpectedly much higher than that of 2-endo-norbornyl sulfonate, which is explained by the 'non-classical' carbenium ion intermediate [9]. The stability of sulfonate is one of the important factors for the photoresist materials. The structures of VS03Rs were characterized by IR, 1H-, 13C-NMR spectroscopy, and elemental analysis.

3.3. Homopolymerization of VS03R

All radical polymerizations of VS03R were conducted in bulk using 2,2'-azobisisobutyronitrile (AIBN) as an initiator (Scheme 2). The results are summarized in Table 2.

The radical homopolymerizability of VS03Rs mainly depends on their sulfonate groups. Primary VS03Rs bearing small alkyl substituents such as VS03Me, VS03Bu, and VS03CF3Et polymerized easily, giving polymers with the number-average molecular weights ($M_n$) of around 30,000 in good yields. On the other hand, VS03CyMe and VS03AdMe having large substituents were reluctant to...
undergo homopolymerizations, producing polymers in very low yields. Secondary VS03Rs with small alkyl substituents such as VS03iPr polymerized below 50 °C, the homopolymerizations of VS03R having large substituents such as VS03Cy, VS03iPr6F, VS03-endo-NB, and VS03Pina didn't occur at any temperatures and gave the hydrolyzed compound, vinyl sulfonic acid.

Homopolymers obtained were identified as the expected poly(VS03R)s by IR and ¹H-NMR spectroscopy. The IR spectra of poly(VS03R)s indicated characteristic sulfonate absorptions at around 1360 cm⁻¹, and no trace of vinyl bond stretching at around 1620 cm⁻¹ was observed. Figure 4 shows the ¹H-NMR spectrum of VS03Me. The ¹H-NMR spectrum consisted of two doublet and doublet-doublet for vinyl protons (δ = 6.18, 6.44, and 6.53 ppm, a singlet for methyl protons (δ = 3.84 ppm) adjacent to oxygen. The ¹H-NMR spectrum of polymer exhibited two broad peaks at 2.2-2.8 and 3.8-4.2 ppm due to the ethylene and methyl protons.

3.4. Copolymerization of VS03R with HFIS

Copolymerization of VS03R with HFIS was studied for the resist formulation (Scheme 3).

![Scheme 3](image)

Table 3 summarizes the results of copolymerizations, where bulk copolymerizations were carried out using an equimolar ratio of VS03R and HFIS at temperature range from 40 to 75 °C for 24 h. After the polymerizations, copolymers obtained were dissolved in acetone and reprecipitated into 50 volumes of hexane twice and water once. All copolymerizations proceeded smoothly, giving the high molecular weight copolymers. However, poly(VS03iPr-co-HFIS) and poly(VS03Cy-co-HFIS) having secondary sulfonate groups were dissolved in water during reprecipitation. Because these secondary VS03Rs are susceptible to hydrolysis and generate the corresponding poly(sulfonic acid). The other copolymers were successfully purified and obtained as white

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Table 3. Characteristics of poly(VS03R-co-HFIS)

Conditions: 1 mol% AIBN, 50 h. Initial concentration of monomers in bulk or in toluene. Determined by GPC (PSt standards, DMF). Polymer composition determined by sulfur analysis. Glass transition temperature measured by DSC. Decomposition temperature measured by TGA under N₂. Isolation yield before precipitation with H₂O. Not determined. Not observed.
powders.

Alfrey-Prices $e$ values are known to be linearly correlated with Hammett $\alpha$ constants and the linear relationship between $e$ values and NMR chemical shifts of vinylic double bonds has been well established [10]. $^{13}$C chemical shifts are a sensitive measure of electron density on carbon atoms [11]. Thus, $e$ values of VS03Rs (Table 1) were estimated from $^{13}$C chemical shifts of the $\beta$-carbon of VS03Rs. The $e$ values of VS03Rs were around 0.9, which indicate a good copolymerizability with monomers having relatively high negative $e$ values [12].

Copolymers were also identified as the expected poly(VS03R-co-HFISt)s by IR and $^1$H-NMR spectroscopy, and elemental analysis. The IR spectra of poly(VS03R-co-HFISt)s exhibited a characteristic O-H bond stretching at 3300 cm$^{-1}$ and a SO$_2$ bond stretching at 1360 cm$^{-1}$. In the $^1$H-NMR spectra, the vinyl protons of VS03R and HFISt at around 6.5 ppm completely disappeared. The copolymer compositions were determined by sulfur analyses. The molar ratios of VS03R and HFISt in the copolymers were around 1 : 4. VS03Rs were characterized by their unexpected low $Q$ values. For example, the $Q$ value of butyl vinyl sulfonate was reported as 0.021 ($e = +0.84$), quite comparable to those of vinyl chloride and vinyl acetate [12]. This unusual character of an unsaturated substituent was observed for the vinyl sulfone as well [13]. It is reasonable to assume that the transition state in growing chain end of VS03R is not stabilized by the expected resonance structures. Due to the low $Q$ value of VS03Rs, only 20% of VS03R were introduced in the copolymers even in the feed ratio of 1 : 1 (VS03R:HFISt).

Thermal properties of the copolymers evaluated by the TGA technique have been listed in Table 3. The TGA traces for typical poly(VS03Bu-co-HFISt)s are shown in Figure 5. It was found that thermal stability largely depended on their structures. First weight loss can be attributed to decomposition of sulfonate. The observed weight-losses were in good agreement with the calculated ones. As mentioned above, secondary alkyl sulfonates decompose easier than primary ones. $\alpha$-Perfluoroalkyl vinyl sulfonates, such as VS03CF3Et and VS03iPr6F solvolyze more slowly than their $\alpha$-hydrogen analogs, because the $\alpha$-carbon is strongly destabilized by the electron-withdrawing CF$_3$ groups bound to it [14]. Therefore, poly(VS03CF3Et-co-HFISt) and poly(VS03iPr6F-co-HFISt) showed higher thermal stability.

![Figure 5. TGA and DSC curves of poly(VS03Bu-co-HFISt)](image)

### 3.5. VUV spectra of poly(VS03R-co-HFISt)

Figure 6 shows the calculated spectra of poly(VS03R-co-HFISt)s, which were obtained by summing up the calculated spectra of VS03Rs and HFISt in proportion to the copolymer compositions. These spectra suggested that all poly(VS03R-co-HFISt)s have high transparency near 157 nm region, and in particular, poly(VS03CF3Et-co-HFISt) and poly(VS03iPr6F-co-HFISt) showed the highest transparency among them. The experimental spectra of these copolymers almost agreed with the calculated spectra with some exceptions (Figure 7). Copolymers have Abs. of 2.3-3.5 µm$^{-1}$ over composition ratios of VS03Rand HFISt of ca. 23 : 77 to 32 : 68. Note that the Abs. of copolymers is greatly decreased by the incorporation of VS03CF3Et and VS03iPr6F resulting in Abs. of 2.5 and 2.3 µm$^{-1}$, respectively, as expected by calculation.

In addition to the influence on electronic states of molecules, incorporation of fluorinated side groups generally provides substantial decrease in Abs. Firstly, fluorinated substituents are inherently transparent in the VUV region. Secondly, it is well known that fluorinated substituents decrease molecular polarizability and weaken intermolecular interactions. Hence, polymers having fluorinated side groups have larger molecular volumes than those expected from calculated van der Waals volumes, and this further reduces the Abs. [6]. This is called ‘dilution effect’. Compared to poly(VSF-co-HFISt), these results indicate that
VSO₃CF₃Et and VSO₃iPr₆F should work as more effective transparent enhancers than VSF. These improvements in transparency are supported by the Abs. of homopolymers (2.1 µm⁻¹ for VSO₃Me and 1.3 µm⁻¹ for VSO₃CF₃Et).

These transparent enhancers are noteworthy in three aspects. First, α-(perfluoroalkyl) vinyl sulfonates are more inert than VSF. Second, hydrophobicity stems from many fluorine groups are successfully compensated by contributions of polar sulfonyl groups while maintaining their transparency. Thus, copolymers containing these units show adequate adhesion to a silicon wafer and good solubility toward common organic solvents. Third, from the industrial point of view, these units are very attractive for their easy preparation. Scheme 4 summarizes the experimental values of Abs. at 157 nm for our representative copolymers.

Figure 6. Calculated VUV spectra of poly(VSO₃R)-co-HFIST

Figure 7. VUV spectra of poly(VSO₃R)-co-HFIST (measured)

These transparent enhancers are noteworthy in three aspects. First, α-(perfluoroalkyl) vinyl sulfonates are more inert than VSF. Second, hydrophobicity stems from many fluorine groups are successfully compensated by contributions of polar sulfonyl groups while maintaining their transparency. Thus, copolymers containing these units show adequate adhesion to a silicon wafer and good solubility toward common organic solvents. Third, from the industrial point of view, these units are very attractive for their easy preparation. Scheme 4 summarizes the experimental values of Abs. at 157 nm for our representative copolymers.

Scheme 4

It is said that a ideal molecular weight for photoresist materials is around 10,000. Thus, solution polymerizations were investigated to obtain lower molecular weights of copolymers. Furthermore, the composition of copolymers is
required to make the copolymers more transparent. And we chose the desired composition of VS03R (40) : HF1St (60) which was considered as much content of transparent unit as possible, while keeping the polymer acid labile enough. From the copolymer composition curve measured on the copolymerization of styrene and butyl vinyl sulfonate [13], which can be regarded as an analog monomer of HF1St and a representative of various VS03Rs, respectively, we determined the appropriate feed ratio of VS03Rs : HF1St were 5 : 1. As a result, under the 1 mol/L monomer concentration and its feed ratio of 5 : 1 (VS03R : HF1St), the molecular weight of polymer obtained was controlled to ca. 15,000 and its copolymer composition ratio of 2 : 3 (VS03R : HF1St).

3.6. Lithographic Evaluation

Partially tert-butoxy carbonylation of poly(VS03iPr6F-co-HF1St) which showed the highest transparency among these copolymers was carried out by reacting the copolymer with di-tert-butyl dicarbonate in the presence of 4-dimethylaminopyridine (DMAP) in acetone. DMAP could be removed completely by several reprecipitations into hexane and water. The protecting ratio of copolymer was roughly optimized to be acid labile. Lithographic evaluation was performed with this acid labile poly(VS03iPr6F40-co-HF1St60-co-t-BOC HF1St32) containing 5 wt% triphenylsulfonium triflate as a photoacid generator. The spin-cast resist film was pre-baked at 100 °C for 60 sec. To evaluate the lithographic characteristics of the resist sensitivity curves, the resist films were exposed using a F2 laser. The resist films were post-exposure baked at 140 °C for 60 sec.

Figure 8 shows the relationship between the exposure dose and the remaining film thickness of the resist. High sensitivity and high contrast characteristics curves were satisfactorily obtained after development using a TMAH aqueous solution. It indicated that the sensitivity and contrast were 5.0 mJ cm⁻² and 10.3, respectively. These findings clearly indicated that this resist system would be a good candidate for 157 nm resist.

4. Conclusion

With a aid of time-dependent density functional theory (TD-DFT) calculations using the B3LYP hybrid functional, poly(VS03R)s with high transparency at 157 nm were developed. Especially, the Abs. of poly(VS03CF3Et) reached to 1.3 µm⁻¹. Various copolymers from VS03Rs and HF1St were also prepared and the Abs. of [poly(VS03iPr6F40-co-HF1St60)] was found to be 2.4 µm⁻¹ at 157 nm.

Partially t-BOC-protected poly(VS03iPr6F40-co-HF1St60-co-t-BOC HF1St32) (Abs. = 2.6) containing 5 wt% triphenylsulfonium triflate functioned as a positive alkaline developable polymer. Its contrast and sensitivity were 10.3 and 5.0 mJ cm⁻², respectively, upon 157 nm irradiation.

References
6. S. Ando, T. Fujigaya, M. Ueda, J.