Synthesis, Characterization and Lithography Performance of Photoacid Generator with Short Perfluoroalkyl Anion

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Summary

A new environmentally friendly photoacid generator (PAG) consisting of diphenyliodonium salt as photoactive cation and fluoroalkyl sulfonium anion as counter ion was synthesized. From FT-IR measurement, it was found that non perfluorooctyl sulfonates (PFOS) PAG from UV irradiation could produce strong acid that subsequently catalyzes the deblocking of a protecting group in copolymer. A positive resist formulation at 248 nm based on the chemically amplified resist mechanism indicated that fluoroalkyl sulfonium anion was capable of providing good image profiles.

Introduction

Chemically amplified resists based on deprotection mechanisms are the pioneering breakthrough for advanced device fabrication. In systems that incorporate chemical amplification, the primary photochemical event generates a catalyst from a photoactive compound that serves to catalyze a cascade of subsequent reactions which in turn change the polarity of the resist in the exposed area. The most popular chemical amplification resist used in DUV lithography uses photoacid generator (PAG) as a photoactive compound to generate acid catalyst that further catalyzes numerous deprotection or cross-linking reactions [1-6].

Photoacid generators (PAG) become a critical component in DUV chemically amplified resist in order to meet the required lithographic performance [7-8]. Among the various classes of ionic and nonionic PAGs that have been developed, one of the most widely used classes of PAGs is the perfluorinated onium salts [9-10]. Recently, commercial and government action have made the use of the most effective PAGs based on perfluorooctyl sulfonates (PFOS) no longer viable. Despite the increased concern with the hazardous nature of some perfluorocarbons (PFCs) [11], they have numerous advantages like high quantum yield of acid generation, good solubility, good thermal stability in resist films, adequate diffusion length, and relative ease of chemical modification [12-13]. Along with this environmental issue, long-chained

perfluorinated sulfonate ester counter ions have problems of limited compatibility with the polymer matrix [14]. The resulting problems include phase separation, non-uniform acid distribution and migration during the baking process, and may eventually lead to an undesirable, premature, and non-uniform deprotection reaction in the chemically amplified resist film, such as T-topping, closure, footing, and excessive line edge roughness. As the feature size is getting smaller, these kinds of problems become increasingly serious.

The environmental issue along with technical issue raised by DUV lithography requires new class of non-PFOS PAGs. There have been several efforts to develop new PAGs. However, most of them have focused on improvement of the photosensitive onium cation side to increase the quantum yield or to improve the absorbance [15-16]. The photoacid generated from PAG is responsible sensitivity, photospeed, resolution and other technical issue related to lithography. To ensure high acidity, high boiling point, and appropriate diffusion length, the structure of counter ion in the ionic photoacid generator is important. By considered design of the counter ion molecule, we plan to improve the distribution of the PAG in the resist and provide appropriate mobility of the photogenerated acid while at the same time addressing environmental issues.

In this paper, we describe the synthesis and characterization of the new PAG with no PFOS. This PAG produce sulfonic acids that contain short perfluoro group that is far fewer than the 9 fluorinated carbons found in PFOS. The alkyl groups introduced to the PAG control the interaction of the PAG with the polymer matrix, which facilitates the uniform distribution and diffusion of the generated acid in the polymeric matrix. A new non-PFOS PAG with alkyl groups and poly(4-hydroxystyrene-*co-t*-butoxycarbonyloxystyrene-*co*-4-trimethylsilylstyrene) were used for a chemically amplified resist system is shown in Figure 1.
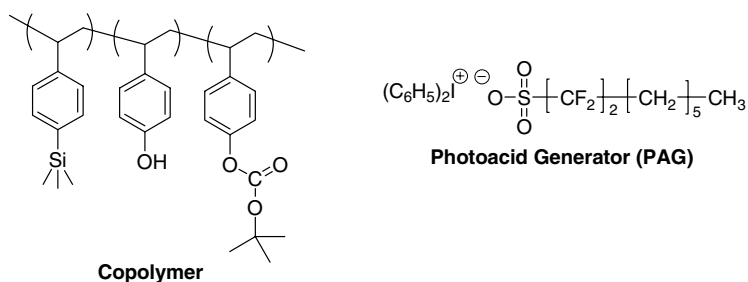

Figure 1

Experimental

Methods
NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Infrared spectra were recorded using a Mattson on a 2020 Galaxy Series FTIR spectrometer. Exposure on 248 nm was carried out using a Nikon 248 nm stepper (NA = 0.42, σ = 0.5) equipped with a KrF excimer laser (Cymer CX-2LS) at Cornell Nanofabrication Facility (CNF).

Materials
1-iodo-2-chlorotetrafluoroethane was purchased from SynQuest Laboratories, Inc. Cl_2 gas (Aldrich), diphenyliodonium chloride (Aldrich), and 1-hexene (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. The other reagents were used as supplied without further purification. Poly(4-hydroxystyrene-*co*-t-butoxycarbonyloxystyrene-*co*-4-trimethylsilylstyrene) used in this study was synthesized by protecting poly(trimethylsilylstyrene-co-hydroxystyrene) with tert-butyldicarbonate. Detailed experimental procedure was described in the reference [17].

Synthesis of non-PFOS PAG with alkyl groups
Synthesis of sodium 2-chlorotetrafluoroethanesulfinate **(1)**
Under nitrogen, a mixture of 1-iodo-2-chlorotetrafluoroethane (25.0 g, 0.15 mol), sodium hydrosulfite (39.1 g, 0.23 mol), sodium bicarbonate (12.6 g, 0.15 mol) was added in to a solvent mixture composed of acetonitrile (110 ml) and water (330 ml). The reaction mixture was stirred at 70 °C for 3 h. The mixture was then poured into a mixture of ethylacetate and brine. The two liquid layers that formed were separated. The organic layer was washed repeatedly with brine and dried with sodium sulfate. Evaporation of the solvent gave a white solid (23.4 g, 70 %), which was purified with recrystallization from isopropanol. ^{19}F NMR (D_2O/CF_3COOH, δ) = -68 (-$ClCF_2$), -128 (-CF_2SO_2Na) ppm.

Synthesis of 2-chlorotetrafluoroethanesulfonyl chloride **(2)**
The sulfinate (10 g, 0.04mol) **(1)** was dissolved in distilled water and cooled to 0-10 °C with an ice. Then chlorine gas was bubbled into this mixture over about 2 h. The resulting yellow mixture was stirred 1 h without external cooling, during which time two liquid layers formed. The oil layer was obtained (4.1 g, 44 %) was used in the next step without further purification. ^{19}F NMR ($CDCl_3/CF_3COOH$, δ) = -67 (-$ClCF_2$), -105 (-CF_2SO_2Cl) ppm.

Synthesis of sodium 2-chlorotetrafluoroethanesulfonate **(3)**
Sodium hydroxide (1.7 g, 0.04 mol) was dissolved in 30 ml distilled water. THF (8 ml) was added and this solution was stirred for 1 h. The sulfonyl chloride (4.0 g, 0.02 mol) **(2)** was added dropwise to the solution. After the addition was complete, the solution was stirred for over 3 h. Then, the mixture was poured into a mixture of ethylacetate and brine. The organic layer was washed with brine and dried with sodium sulfate. The organic solution was concentrated to dryness on a rotary evaporator giving the pure yellow solid (1.4 g, 30 %). The sulfonate was further purified with recrystallization from isopropanol. ^{19}F NMR (D_2O/CF_3COOH, δ) = -68 (-$ClCF_2$), -116 (-CF_2SO_3Na) ppm; IR 1070 (s, SO_3Na) cm^{-1}.

Synthesis of sodium hexyltetrafluoroethanesulfonate **(4)**
A mixture of sodium sulfonate (2 g, 0.008 mol) **(3)**, 1-hexene (0.9 g, 0.01 mol), ammonium persulfate (1.9 g, 0.008 mol), and sodium formate (0.6 g, 0.008 mol) in 20ml dry dimethylformamide (DMF) was stirred at 40 °C for 4 h. The mixture was poured into water and then extracted with ethylacetate. The extract was washed with aqueous sodiumbicarbonate and brine and dried over sodium sulfate. Evaporation of the solvent gave the pure viscous liquid (0.4 g, 15 %). ^{19}F NMR ($CDCl_3/CF_3COOH$,

δ) = -114 (-CH$_2$CF$_2$), -116 (-CF$_2$SO$_3$Na) ppm; ^{1}H NMR (CDCl$_3$, δ) = 0.82 (m, 3H, CH$_3$), 1.25-1.6 (m, 8H, 4CH$_2$), 3.2 (m, 2H, CH$_2$CF$_2$) ppm; IR 1070 (s, SO$_3$Na) cm^{-1}.

Synthesis of diphenyliodonium sodium hexyltetrafluoroethanesulfonate **(PAG) (5)**
Perfluoroalkyl sulfonate (1.0 g, 0.004 mol) **(4)** and diphenyliodonium chloride (1.1 g, 0.004 mol) in methanol were stirred at 50 °C for 4 h under a dark condition. The mixture was concentrated on a rotary evaporator and the crude solid was extracted with ethylacetate to give a gummy solid (0.8 g, 40 %). ^{19}F NMR (CDCl$_3$, δ) = -114 (-CH$_2$CF$_2$), -116 (-CF$_2$SO$_3^-$) ppm; ^{1}H NMR (CDCl$_3$, δ) = 0.82 (m, 3H, CH$_3$), 1.25-1.6 (m, 8H, 4CH$_2$), 3.2 (m, 2H, CH$_2$CF$_2$), 7.3 (m, 4H, Ar-H), 7.5 (m, 2H, Ar-H), 7.9 (m, 4H, Ar-H) ppm; IR 3100 (s, Ar-H) cm^{-1}.
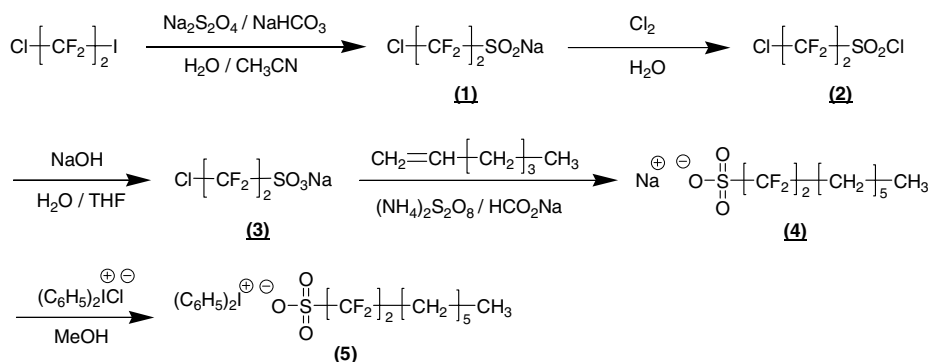
Scheme 1

Photoacid generation by FT-IR measurement
A typical resist formulation used for FT-IR experiment consists of 7 % of poly(*t*-butoxycarbonyloxystyrene), 3.5 % of PAG and 90 % of PGMEA. The mixture was stirred until the components dissolved and then filtered on to double side polished silicon wafer. The solvent was removed by gentle nitrogen blow. The resist coated wafers were baked at 90 °C for 30 sec. FT-IR spectrum of unexposed resist with PAG was recorded. The wafers were then exposed using broad band UV lamp [UVEXSSCU110B (250-750 nm; Total Lamp Power = 100 mW/cm^2)] for 120 sec. The samples were baked at 90 °C for 60 sec. FT-IR measurement was carried out again on the exposed wafer. The difference in absorption of carbonyl peak at 1763 cm^{-1} before and after exposure was monitored.

Resist formulation with new PAG
A typical formulation for 100 g of resist solution consists (total weight 11-20 % of solids), 9-11 % of poly(4-hydroxystyrene-*co-t*-butoxycarbonyloxystyrene-*co*-4-trimethylsilylstyrene) with 30 % of 4-*t*-butoxycarbonyloxystyrene, 2-9 % of PAG, 0.06 % of trioctylamine (TOA) and 80-88 % of propylene glycol methyl ether acetate (PGMEA) or PGMEA-isopropanol (60-20 %) mixture. The mixture was stirred until the components dissolved. The resist solution was filtered through 0.2 μm membrane filter.

Patterning of the polymer resist

The resist solution was spin-coated (2000 rpm) onto silicon wafers that are primed with HMDS. The resist coated wafer was baked at 115 °C for 60 sec. The coated wafers were exposed using 248 nm stepper. The wafers were post exposure baked at 115 °C for 60 sec and developed using 0.52 N tetramethylammonium hydroxide (TMAH) solution for 2 sec. The wafers were rinsed with de-ionized water and dried. The images were analyzed by optical microscope.

Results and Discussion

The synthetic steps involved in the preparation of the new PAG with perfluoro alkyl chain are summarized in scheme 1. The procedure used by Hu and Feiring [18-19] for perfluoralkyl sulfonate was modified and used for the synthesis of new PAG. The products from each step were isolated and characterized. Proton and fluorine NMR spectra agreed well with the structures of all compounds as expected. 1-iodo-2-chlorotetrafluoroethane can be readily converted to its sodium 2-chlorotetrafluoroehtanesulfinate (**1**) with sodium dithionite and soidumbicarbonate in high yield. The isolation of sodium sulfinate from inorganic impurities can be achieved using isopropyl alcohol because of the different solubility between both of them. The dehalogenosulfiantion strongly depends on the energy of the bond to be broken ie., $-CF_2-I>$ $-CF_2-Br \sim CCl_3>$ $-CFCl_2$ [20]. The sulfination reaction was performed in acetonitrile at 70 °C for 3 h. The introduction of chlorine gas to the aqueous solution of sulfinate (**1**) under ice-cold condition for more than 2 h gives the corresponding yellow sulfonyl chloride (**2**) which is transformed to sodium sulfonate (**3**) on reaction with sodium hydroxide in aqueous THF.
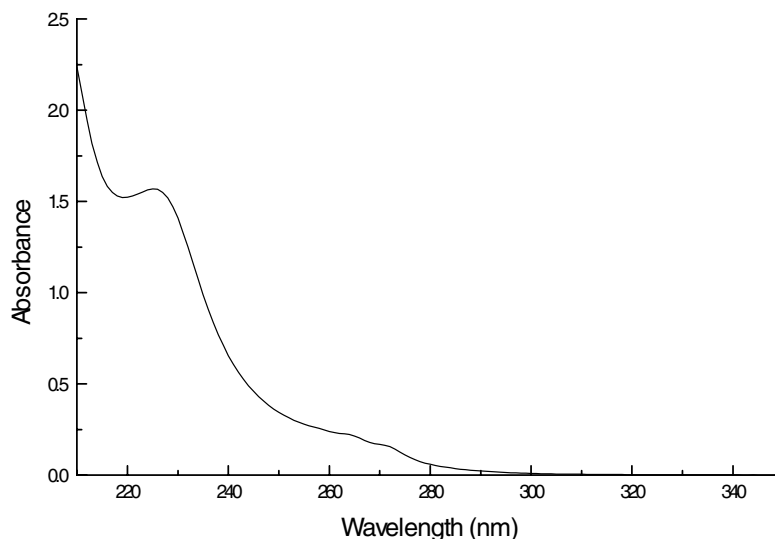

Figure 2. UV spectrum of new PAG in methanol

The addition reaction of hexene to sodium sulfonate (**3**) in the presence of suitable oxidizer such as $(NH_4)_2S_2O_8$ results in the alkylated product (**4**). Finally the anion exchange reaction of (**4**) with diphenyliodonium chloride in methanol results a new ionic PAG (**5**).

Figure 2 shows UV spectrum of new ionic non-PFOS PAG. The absorption at the maximum wavelength (226 nm) which was $\pi \rightarrow \pi^*$ electronic transition energy of the iodonium salt was observed. The same absorption was obtained from the diphenyliodonium chloride or diphenyliodonium triflate.

The resist coated with PAG should produce photoacid if it is exposed to DUV radiation. The generation photoacid can be understood by monitoring specific absorption peak by FT-IR measurement. FT-IR measurement of poly(*t*-butoxycarbonyloxystyrene) resist system was conducted to confirm an acid production from the new PAG with alkyl groups. As shown in Figure 3, a strong absorption band for phenyl and carbonyl group appeared around 3000 and 1750 cm^{-1}, respectively. An irradiation of polymer film containing the PAG with UV light liberates an acid species that subsequently deprotects the t-butyl carbonyl group present in the polymer. The hydroxyl group of deprotected copolymer exhibits O-H stretching at 3500 cm^{-1}. Loss of the tert-butoxycarbonyl group results in a large polarity change in the exposed areas of the film. The control experiments performed using the polymer alone dose not result any change in the absorption of carbonyl peak before and after exposure. The films were smooth so the alkyl groups incorporated in PAG can inhibit the formation of undesirable crystalline domains in the polymer matrix and give better solubility and miscibility with photoresist materials.
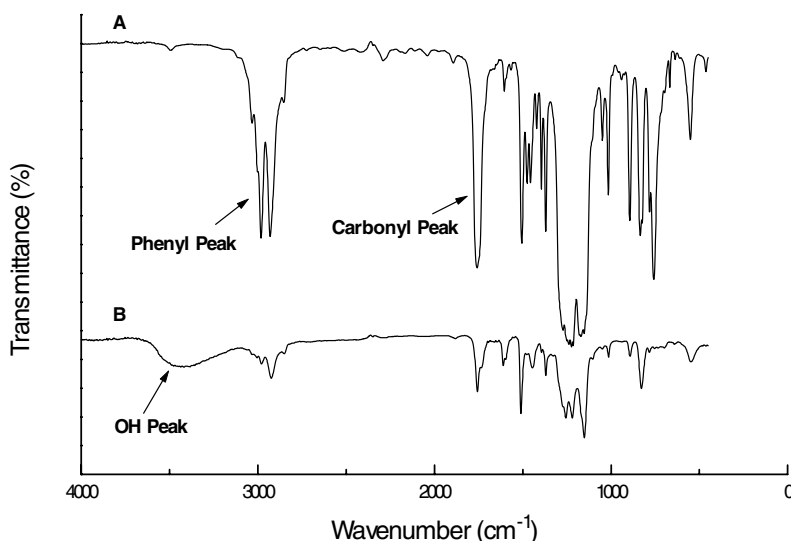

Figure 3. FT-IR spectra of polymer with PAG before (A) and after (B) UV irradiation

The compositions of the resist solution and the processing conditions used for lithography were described in the experimental section. The wafers coated with resist formulation were exposed to 248 nm radiation using a Nikon 248 nm stepper. A mask containing a pattern ranging from 0.2 μm to 2 μm was projected onto the imaging

layer. Areas on the wafer were exposed for different amounts of time, so that the imaging layer was exposed to energies of 2 to 56 mJ/cm^2. After exposure the wafer was then baked at temperature of 115 °C for 60 sec. Latent image was appeared during post exposure bake and then the wafer was immersed in a TMAH solution for few seconds and then rinsed with water. The areas of imaging layer exposed to the UV radiation were washed away by the developer solution and the areas unexposed to UV radiation were left on the wafer. The images obtained using optical microscope for the copolymer resist with non-PFOS PAG with alkyl groups is shown in Figure 4. The photoresist with non-PFOS PAG showed promising image capability on the 248 nm exposure test. An attempt for the performance of non-PFOS PAG with other wavelength source (EUV) is in progress.
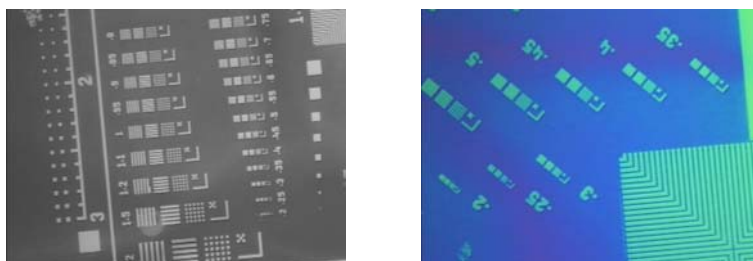

Figure 4. Optical micrographs obtained from copolymer with PAG [PAG (9.6 wt %), TOA (0.006 wt %), Post Apply Bake (PAB) (115 °C/ 60 sec), Post Exposure Bake (PEB) (115 °C/ 60 sec), Exposure = 248 nm; E_0 (dose to clear)= 34 mJ/cm^2; Development = 0.52 N TMAH, 2 sec]

Conclusions

A ionic photoacid generator has been developed that is based upon fluoroalkyl sulfonic acids that contain far fewer than the 9 fluorinated carbons found in PFOS. The synthesis of PAG involves several steps in reasonably good yields with appropriate purity using commercially available reagents. Preliminary screening in a positive resist formulation at 248 nm indicates that this anion is capable of providing good image profiles comparable to conventional PAG. PAG with short perfluoroalkyl groups should have high combustibility and no bioaccumulation. The new PAG with no PFOS improved the homogeneous distribution of the PAG in the resist and addressed environmental issues of the existing PFOS PAG. Therefore, this non-PFOS PAG is expected to be environmentally friendly.

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