Cyclopropyl-containing Photoacid Generators for Chemically Amplified Resists

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Several cyclopropyl-containing photoacid generators (PAGs) were synthesized in order to reduce absorbance at 193 nm and induce the photobleaching effect. From the GC–mass experiment, cleavage of S–C(cyclopropyl) which is more preferential than that of S–C(phenyl) results in photobleaching effect. The resist containing cyclopropyldiphenylsulfonium triflate gave better resolution than the resist containing the conventional PAG, triphenylsulfonium triflate.

Triphenylsulfonium salts[1] have found widespread use as photoacid generators for the cleavage of acid labile groups in chemically amplified resists. However, these salts absorb so much light at 193 nm that there have been a lot of trials to adapt the more transparent photoacid generators[2] (PAGs) to 193-nm resist systems. In many cases, they have tried to substitute alkyl groups for the aryl groups in the sulfonium salts. But alkyl-substituted sulfonium salts often had low thermal stability or poor solubility in the matrix resin so they could not be applicable for practical use. Moreover, transparent alkyl sulfonium salts are not so photoactive toward acid generation because of the high strength of the S–alkyl bond[3] (namely, the instability of an alkyl radical).

We report here on the introduction of the cyclopropyl group[4] into the PAGs to give the photobleaching property at 193 nm. The small cyclopropyl radical, made from the photolysis, can be converted to the more stable allyl radical and vaporize easily. In this case, the cyclopropyl-containing PAGs become more photoactive due to the stability of the allyl radical generated from the cleavage of S-C(cyclopropyl).

Four PAGs with a cyclopropyl group were synthesized. A solution of 0.05 mol of cyclopropylphenyl sulfide (7.5 g) and 0.05 mol of alkyl halide in 20 mL of nitromethane was stirred under nitrogen. The flask was shielded from light, and 0.05 mol of silver trifluoromethanesulfonate (12.8 g) was added. After the mixture was stirred at 50–60 °C for 18 h, it was filtered, and the combined solution was recrystallized in methylene chloride/ether solution. The white crystal was collected, washed with ether, and dried under reduced pressure. Cyclohexylcyclopropylphenylsulfonium triflate (ChCpPSTf), cyclopropylnaphthalene-2-ylmeththylphenylsulfonium triflate (CpNPSTf), and cyclopropylphenlypropylsulfonium triflate (CpPPSTf) were obtained in a yield of 67–75%.[5] The synthetic scheme for the preparation of these cyclopropyl-containing PAGs is shown in Figure 1. Cyclopropyldiphenylsulfonium triflate (CpDPSTf) was synthesized by the method reported in the literature.[6]

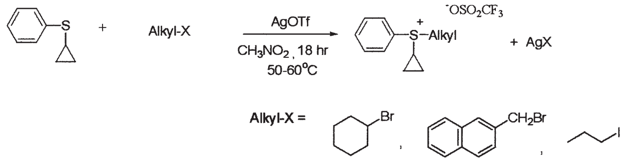


Figure 1. The synthetic scheme for preparation of cyclopropyl-containing sulfonium triflate.

Table 1 shows the UV absorbances[7] of the films measured before and after irradiation of 50 mJ/cm^2 exposing dose. ChCpPSTf was excluded from the further experiments since it was obtained as a liquid. Resist solutions were prepared by dissolving poly(*tert*-butyl methacrylate) (PTBMA) and the PAGs in cyclohexanone. The absorbances of cyclopropyl-containing sulfonium triflates (resists B, C, and D) are lower than that of the conventional PAG (resist A). Also the new PAGs show bleaching effect. The absorbance decreases after exposure. On the other hand, the absorbance of the conventional PAG, TPSTf, increases after exposure because the recombination products such as phenylthiophenylbenzene are major products.

In order to understand the bleaching mechanism, product analysis of the irradiated resist solution containing CpDPSTf was performed by the GC-mass method[8] as shown in Figure 2. There are five characteristic peaks, 8.7% of cyclopropylphenyl

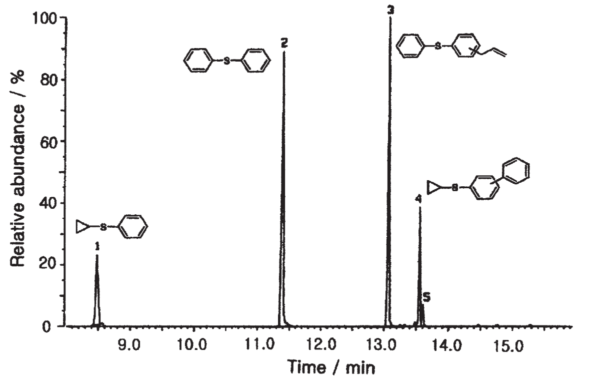
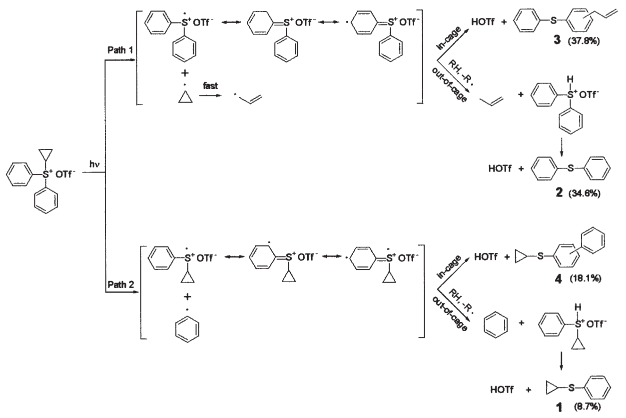


Figure 2. GC-mass spectrum of products after 254-nm irradiation of 10 mM CpDPSTf solution in acetonitrile.

Table 1. The absorbances at 248 nm and 193 nm of PAGs before and after exposure

Resist	PAG	Absorbance/μm^{-1} at 248 nm			Absorbance/μm^{-1} at 193 nm		
		Before exposure	After exposure	ΔA/%	Before exposure	After exposure	ΔA/%
A	TPSTf	0.195	0.229	+17.0	0.839	0.855	+1.9
B	CpDPSTf	0.102	0.080	−21.2	0.808	0.698	−13.6
C	CpNPSTf	0.268	0.207	−22.7	0.695	0.573	−16.9
D	CpPPSTf	0.036	0.031	−13.1	0.422	0.401	−5.0



Scheme 1. Plausible decomposition mechanism of CpDPSTf upon exposure.

sulfide (1), 34.6% of diphenyl sulfide (2), 37.8% of allylphenylthiobenzene (3), 15.1% of cyclopropylthiophenylbenzene (4), and 3.0% of the shoulder peak (5), which is another isomer of cyclopropylthiophenylbenzene. There are also very minute amounts of other products. The first two peaks 1 and 2 came from direct photolysis and the latter three peaks 3, 4 and 5 came from the recombination reactions.

The plausible decomposition mechanism of CpDPSTf is depicted in Scheme 1. When the PAG is irradiated, the homolytic cleavage of the sulfur–carbon bond leads to the formation of a cation-radical on the sulfur–containing fragment and a neutral radical. And the homolysis must be strongly affected by the stability of both radicals. The diphenylsulfonium cation radical can be much more stabilized than the cyclopropylphenylsulfonium cation-radical because the former has more resonance forms. The cyclopropyl radical is known to be converted very fast to more stable allyl radical[9] and the allyl radical is certain to be more stable than phenyl radical. From these two reasons, the path 1 is expected to be predominant over the path 2. The mechanism is consistent with the results of the GC–mass experiment.

Two resist solutions[10] were formulated by dissolving the polymer (Figure 3, 15 wt% polymer in propylene glycol monomethyl ether acetate) and TPSTf or CpDPSTf (1 wt% relative to the resin), and then the solutions were filtered with a 0.2 μm teflon membrane filter. Figure 4 shows the comparison between resist E, the resist with the conventional PAG, and resist F, the resist with the photobleachable PAG. There are two distinguishing features. First, the side-wall shape of resist F is relatively rectangular while that of resist E is slightly sloped. Generally, the resists containing TPSTf show a somewhat tapered pattern because of the strong absorbance. Second, at the pattern of 120 nm, comparing with the shape of resist E, there is a notable improvement in the shape of resist F. In the case of resist E, even though we increased the dose of exposure and developed for a longer time, the scum did not disappear. The main reason of these differences between the two resists is related to the bleaching effect of CpDPSTf. The strong absorbance of TPSTf prevents the light from reaching the bottom of the resist, leading to scum at the resolution limit. But the photobleaching effect of CpDPSTf makes the light go through to the bottom of the resist, and the exposed region be dissolved clearly. As a result, the photoresist using CpDPSTf showed better performance than the resist using TPSTf in the finer pattern.

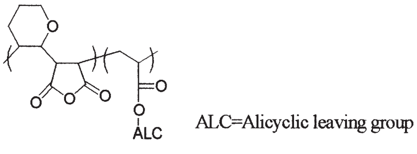


Figure 3. SAS-4.

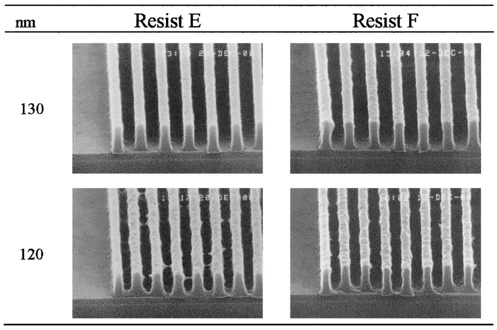


Figure 4. SEM images of the two resists with TPSTf (resist E) and CpDPSTf (resist F) with a each thickness of 0.4 μm at a dose of 10 mJ cm^{-2}.

In conclusion, four PAGs containing a cyclopropyl group have been developed. These novel PAGs show less absorbance at 193 nm than the conventional PAG, TPSTf. Moreover, the cyclopropyl-containing PAGs show the photobleaching effect, while TPSTf shows the antiphotobleaching effect. From the GC–mass experiment of CpDPSTf, cleavage of S–C(cyclopropyl) is much more preferential than that of S–C(phenyl), and this cleavage results in the photobleaching effect. The resist containing CpDPSTf gave better resolution than that containing TPSTf which has been widely used.

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References and Notes

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5 Alkylcyclopropylphenylsulfonium triflate was obtained in a yield of 67–75%. ChCpPSTf: ^{1}H NMR ($CDCl_3$, ppm): δ 0.8–1.0 (4H, m), 1.0–1.3 (6H, m), 1.7–2.0 (5H, m), 3.9 (2H, m), 7.7–8.0 (5H, m);^{19}F NMR: singlet. CpPPSTf: ^{1}H NMR ($CDCl_3$, ppm): δ 1.0–1.2(4H, m), 1.25(3H, m), 1.6(1H, m), 1.75(3H, m), 3.75 (1H, m), 3.85 (2H, m), 7.7–8.0 (5H, m); ^{19}F NMR: singlet. CpNPSTf: ^{1}H NMR ($CDCl_3$, ppm): δ 0.9(1H, m), 1.1(1H, m), 1.4(2H, m), 3.75 (1H, m), 5.2(1H, d), 5.4(1H, d), 7.4–8.0 (10H, m); ^{19}F NMR: singlet.

6 F. G. Kathawala, U. S. Patent 4233292 (1980). CpDPSTf was obtained in a yield of 82.5% as a white crystal. ^{1}H NMR ($CDCl^3$, ppm): δ 1.4 (2H, m), 1.65 (2H, m), 3.95 (2H, m), 7.7–8.0 (10H, m);^{19}F NMR: singlet.

7 UV spectra were recorded as spin-coated films on quartz plates with a Hewlett-Packard Model 8453 spectrophotometer. Four resist solutions were made by dissolving 0.2 g of poly(*tert*-butyl methacrylate) (PTBMA) and 5 wt% of a PAG in cyclohexaneone. These solutions were filtered through a 0.2 μm filter and spin-coated onto quartz plates. For each sample, the UV absorbance was observed before and after exposure using a mercury-xenone lamp. Absorbance data were normalized to one micron and obtained by subtracting the absorbance of the PTBMA film from the observed data.

8 Steady-state irradiation was performed in a Rayonet Photochemical Reactor equipped with RPR 254-nm lamps from the Southern New England Ultraviolet Co. Surpasil quartz cells (10 mm × 10 mm) were used in these experiments. Each 10 mM solution of TPSTf and CpDSPTf in 3 mL of degassed acetonitrile was irradiated with 254-nm light for 3 min. The irradiated solutions were diluted with acetonitrile and analyzed by GC–mass. Gas chromatography was taken with HP6890 plus, and mass analysis was taken with JEOL SX102A.

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10 The resist solutions were coated to yield 0.4 μm-thick films on silicon wafers and soft-baked at 120 °C for 90 s. Exposure was carried out with an ArF stepper (ISI, NA = 0.6) using a conventional illumination method. Exposed resists were baked at 110 °C for 90 s on a hot-plate and developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution for 60 s.

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