Novel Acid Amplifier Generating Disulfonimide as Superacid

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Disulfonimide acid amplifier which produces superacid was newly designed and synthesized. This compound exhibited high acid generation efficiency and thermal stability on a polymer film. Further, this compound enhanced the sensitivity in the positive chemically amplified photoresist system.

Keywords: Disulfonimide, Acid amplifier, Superacid, Photoresist

1. Introduction

Acid amplifiers (AAs) are precursor compounds which produce more acid via acid-catalyzed reactions (Fig. 1) [1]. The decomposition of AA is mostly initiated by a trigger acid produced by photoacid generator (PAG).

![Fig. 1. Schematic reaction process of acid amplifier (AA).](image)

Previously, a variety of AAs have been developed and reported to be applied in photopolymer systems utilizing acid-catalyzed reactions (Fig. 2) [2-7].

![Fig. 2. Representative structures of AA.](image)

Their utilization has also been proposed for chemically amplified photoresists consisting of PAG and an acid-labile polymer. Especially, there is much interest in the requirements for high sensitive EUV resists in the microelectronics industry because of a limited usage of high power EUV light source [8].

Typical AAs generate weak sulfonic acids like arylsulfonic acid due to the lack of thermal stability. Recently, AAs generating strong acids called superacid [9] have been reported (e.g., perfluoroalkyl sulfonic acid and fluorinated alkyl sulfonic acid (Fig. 3)) [10]. However, these kinds of AAs generating superacid have been limited in investigation due to their synthetic difficulty and thermal unstability.

![Fig. 3. Examples of AAs generating superacid.](image)

Bis(perfluoroalkyl)sulfonylimides have also been known for its superacidic properties matching or exceeding the acid strength of perfluoroalkyl sulfonic acids [9]. These acids have been found to be useful, for example, not only as a deprotection catalyst for chemically amplified photoresist [11] but also as fuel cell electrolytes, esterification catalysts and polymerization catalysts for...
cationically-sensitive monomers such as epoxy resins [12]. Nevertheless, acid amplifiers generating disulfonimide have not been reported so far.

Herein, we describe the design and synthesis of a novel acid amplifier to produce bis(perfluoroalkyl)sulfonylimide as the superacid. The acid efficiency and thermal stability of this compound was investigated on a polymer film. Further, this compound was applied to the positive chemically amplified photoresist to examine the influence of sensitivity.

2. Experimental

2.1. General methods

$^1$H NMR spectra were measured on a Varian Gemini 300 at 300 MHz. $^{19}$F NMR spectra were measured on a Varian Gemini 300 at 282 MHz.

Absorption spectra in the UV-Vis region were measured on a Carry-5 spectrophotometer (Varian).

2.2. Materials

2.2.1. 2-(3-Oxo-3-phenylpropyl)isoindoline-1,3-dione (1a) [13]

![1a]

To a solution of phthalimide potassium salt 11.0 g (59.2 mmol) in toluene 100 mL, 3-chloropropiophenone (10.0 g, 59.3 mmol) was added and the reaction mixture was stirred at 100 °C for 5 h. The reaction was cooled at room temperature. And separated crystals were collected by filtration. The crystals were washed with hexane. Thus, 12.2 g of 1a was obtained (yield: 73.7%).

$^1$H NMR (300 MHz, CDCl$_3$) δ=7.89-7.73 (m, 2H), 7.96-7.70 (m, 6H), 7.56-7.43 (m, 3H), 4.15 (t, J=7.2 Hz, 2H), 3.43 (t, J=7.2 Hz, 2H).

2.2.2. 2-(2-Phenyl-1,3-dioxolan-2-yl)isoindole-1,3-dione (1b)

![1b]

To a solution of phthalimide potassium salt 11.0 g (59.2 mmol) in toluene 100 mL, 3-chloropropiophenone (10.0 g, 59.3 mmol) was added and the reaction mixture was stirred at 100 °C for 5 h. The reaction was cooled at room temperature. And separated crystals were collected by filtration. The crystals were washed with hexane. Thus, 12.2 g of 1a was obtained (yield: 73.7%).

$^1$H NMR (300 MHz, CDCl$_3$) δ=7.89-7.73 (m, 2H), 7.96-7.70 (m, 6H), 7.56-7.43(m, 3H), 4.15 (t, J=7.2 Hz, 2H), 3.43 (t, J=7.2 Hz, 2H).

2.2.3. 2-(2-Phenyl-1,3-dioxolan-2-yl)ethanamine (1c)

![1c]

To a solution of 1b (2.22 g, 6.86 mmol) in MeOH, hydrazine monohydrate (687 mg, 13.7 mmol) was added and the reaction mixture was refluxed for 2 h. The mixture was filtered through a Celite and then concentrated. Potassium hydroxide in MeOH solution was poured into the mixture. The mixture was filtered through a Celite and then concentrated repeatedly. Thus, 1.11 g of 1c was obtained (yield: 83.7%).

$^1$H NMR (300 MHz, CDCl$_3$) δ=7.37-7.26 (m, 5H), 4.03 (t, J=6.6 Hz, 2H), 3.76 (t, J=6.6 Hz, 2H), 2.74 (t, J=6.6 Hz, 2H), 2.07 (t, J=6.6 Hz, 2H).

2.2.4. $N$-[2-(2-Phenyl-1,3-dioxolan-2-yl)ethyl]-1,1,1-trifluoromethanesulfonamide (1d)

![1d]

To a solution of 2-(2-phenyl-1,3-dioxolan-2-yl)ethanamine (5.20 g, 26.9 mmol) in chlorobenzene (100 mL), triethylamine (13.6 g, 134 mmol) was added and the reaction mixture was stirred at 0 °C under nitrogen. Trifluoromethanesulfonic anhydride (15.2 g, 53.9 mmol) was slowly dropped into the cooled solution. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with sat. NaHCO$_3$ aq. solution and the resulting biphasic mixture was extracted with ethyl acetate. The organic layer was washed with H$_2$O and a brine, dried with MgSO$_4$, and then concentrated. The crude product was purified by silica gel chromatography (gradient elution of 9-17% ethyl acetate-hexanes), thereby obtaining 4.81 g of 1b (yield: 33.9%).

$^1$H NMR (300 MHz, CDCl$_3$) δ=7.89-7.73 (m, 2H), 7.70-7.67 (m, 2H), 7.46-7.43 (m, 2H), 7.30-7.20 (m, 3H), 4.03 (t, J=6.9 Hz, 2H), 3.87 (t, J=6.6 Hz, 2H), 3.75 (t, J=6.6 Hz, 2H), 2.32 (t, J=6.9 Hz, 2H).
The design of AAs requires the following three key points [1].

To determine the acid generation amount, the solutions were spin-coated on silicon wafer, and prebaked at 100 °C for 90 s to give a film thickness of 100 nm. The film was exposed by EB (60 keV), followed by Post Bake (90, 110, 130 °C respectively, 90 s).

The resist layer was dissolved in the solvent and an acid indicator dye (imidazo-oxa carbocyanine dye) was added into the THF solution. The relative acid amount was observed by measuring the UV absorbance shift at 485 nm (Fig. 5).

Fig. 5. UV/vis absorption spectral changes of resist following the EB exposure and extraction using an organic solvent containing an acid-sensitive dye.

2.4. Photosensitivity characteristics

Resist samples were prepared by mixing 10 wt% PAG 7, 1 wt% tri-n-octylamine (Base), polymer of tert-butyldimethylacrylate / γ-butyrolactone methacrylate 6 (m/n=50/50), and mixed solvent of propylene glycol methyl ether acetate and propylene glycol methyl ether (50/50, v/v). AA 1 (0, 4.2, 8.4, 12.6 wt%) was added by replacing the polymer. AA 3 was added by equal molar concentration of AA 1 (Fig. 4).

3. Results and discussion

3.1. Design of AA compounds with disulfonimide

The design of AAs requires the following three key points [1].
1. Thermal stability under the condition without an acid, at least within the process of photolithography.
2. Autocatalytic acid generation in the presence of a trigger acid.
3. Strong acid production enough to participate in the photopolymer system such as decomposition of polymers or polymerization of monomers.

Based on preliminary examination, we have chosen \( \beta \)-ketal among various structures of acid amplifiers. And we designed AA 1 of \( \beta \)-ketal disulfonylimide, which is bis(trifluoromethane)sulfonylimide, to generate superacid (Fig. 6) and was synthesized in five steps (Scheme 1). On the other hand, we were unable to synthesize the \( \beta \)-ketal with trifluromethanesulfonate 2 due to the lack of thermal stability.

![Fig. 6. Novel design of acid amplifier generating superacid.](image)

**Scheme 1.** Synthetic scheme of preparation of acid amplifier 1.

3.2. Efficiency of acid generation and thermal stability at resist film

In order to study the efficiency of acid generation of AA 1 compared with AA 3, we evaluated the amount of acid generation of a resist film by an acid indicator. The film was irradiated by EB exposure, followed by Post Bake at 90, 110, 130 °C respectively for 90 s. And thermal stability of the resist film was also confirmed by Post Bake experiment without exposure.

Figure 7 shows that \( \beta \)-ketal disulfonylimide 1 serves as an acid amplifier sufficiently. This compound enhanced the acid efficiency by 2.5 to 5.1 times compared to a case without addition. And AA 1 revealed an efficiency almost similar to AA 3 at PEB 130 °C.

And also, AA 1 was stable to be useful within the temperature range typically used during Post Bake (90-130 °C). Compared with AA 2, the thermal stability of this compound can be attributed to prevention of nucleophilic attack, owing to the steric hindrance or hydrophobic effect of bis(perfluoroalkane)sulfonylimide substitution.

![Fig. 7. Acid generation efficiency and thermal stability of AA 1 and 3 on polymer film.](image)

3.3. Photosensitivity characteristics

Recently, tert-alkylester acrylated based acid-labile polymers, which have low reactivity compared to acetal styrene polymer, have been widely used in photoresists. However, in order to decompose tert-alkylester acrylated polymer 6, very strong acids are required. Thus, the effect of AA 1 loading on resist sensitivity was investigated on tert-alkylester polymer film, which includes PAG 7 (Table 1).

Figure 8 shows the contrast curve of the resist on irradiation by ArF exposure. The sensitivity was strongly affected in the presence of AA 1. We confirmed that the addition of AA 1 (12.6 wt%) in the resist formulation enhanced the sensitivity of the resist by 1.7 times. Therefore, it is plausible that this compound accelerates the decomposition of tert-alkylester polymer effectively, suggesting that this acid proliferation reaction of 1 proceeds in the resist film as shown in Scheme 2.
Table 1. Component of resist films.

| ter-Alkylester /Lactone Methacrylate Polymer | PAG | AA | Amine | Owt% | 1.0w% |
|--------------------------------------------|-----|-----|-------|------|-------|
| 89.0 w%                                    | 10.0 w% | 0.0 w% | 1.0 w% |
| 84.8 w%                                    | 10.0 w% | 1.0 w% | 1.0 w% |
| 80.6 w%                                    | 10.0 w% | 1.0 w% | 1.0 w% |
| 76.4 w%                                    | 10.0 w% | 1.0 w% | 1.0 w% |

Fig. 8. Contrast curve of resist films. The film was exposed at 193 nm and baked at 110 °C for 90 sec, and then developed with a 2.38% aqueous TMAH solution.

Scheme 2. Plausible reaction process of chemically amplified photosensitive including 1.

4. Conclusions

In this paper, a novel acid amplifier 1 which generates disulfonylimide was designed and synthesized to present new potentiality for an acid catalyzed reaction of the photopolymer system. This compound reveals a high acid efficiency and thermal stability under commonly used photosensitive process conditions. Furthermore, this acid amplifier which generates superacid shows good sensitivity at the positive chemically amplified photosensitive system. Thus, β-ketal disulfonylimide as an acid amplifier has a potential to be applicable to practical photosensitive materials. Further work is in progress to introduce other photosensitive systems such as cationic polymerization catalysts for epoxy monomers.

References
1. K. Ichimura, Chem. Rec., 2 (2002) 46.
2. H. Ito and K. Ichimura, Macromol. Chem. Phys., 201 (2000) 132.
3. K. Ichimura, K. Arimitsu, and K. Kudo, Chem. Lett., 24 (1995) 551.
4. (a) S. Noguchi, K. Arimitsu, K. Ichimura, and K. Kudo, J. Photopolym. Sci. Technol., 10 (1997) 315. (b) T. Ohfuji, M. Takahashi, M. Sasago, S. Noguchi, and K. Ichimura, J. Photopolym. Sci. Technol., 10 (1997) 551. (c) S.-W. Park, K. Arimitsu, K. Ichimura, and T. Ohfuji, J. Photopolym. Sci. Technol., 12 (1999) 293. (d) T. Naito, T. Ohfuji, M. Endo, H. Morimoto, K. Arimitsu, and K. Ichimura, J. Photopolym. Sci. Technol., 12 (1999) 509.
5. S. Lee, K. Arimitsu, S.-W. Park, and K. Ichimura, J. Photopolym. Sci. Technol., 13 (2000) 215.
6. K. Arimitsu, K. Kudo, H. Ohmori, H. Ito, and K. Ichimura, Chem. Mater., 11 (1999) 2119.
7. S. A. Kruger, S. Revure, C. Higgins, S. Gibbons, D. A. Freedman, Y. Wang, T. Younkin, and R. L. Brainard, J. Am. Chem. Soc., 131 (2009) 9862.
8. V. Bakshi (Eds.), “EUV lithography”, SPIE and John Wiley & Sons, Inc., (2009).
9. The term “superacid” in this paper refers to a superacidic compound, which can be defined as a compound having higher acidity than H2SO4 in a particular medium (e.g., gas phase or some solvent).
10. (a) S. A. Kruger, C. Higgins, B. Cardineau, T. R. Younkin, and R. L. Brainard, Chem. Mater., 22 (2010) 5609. (b) K. Hosoi, B. Cardineau, S. Kruger, K. Miyachi, and R. Brainard, J. Photopolym. Sci. Technol., 13 (2000) 215.
11. D.-K. Lee, X. Ma, W. M. Lamanna, and G. Pawlowski, Proc. SPIE, 4690 (2002) 169.
12. R. D. Howells, W. M. Lamanna, A. D. Fanta, and J. Wadell, US Patent 5874616 (1995).
13. R. E. Davies and G. Powell, J. Am. Chem. Soc., 67 (1945) 1466.