Photobleaching Photoacid Generator

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A cyclopropyl group was introduced into the photoacid generator in order to give the photobleaching property at 193 nm. Cyclopropyldiphenylsulfonium trifluoromethanesulfonate (CpDP-Tf) was synthesized for this photobleaching effect. This compound is stable up to 165 °C. The absorbance of CpDP-Tf at 193 nm decreases upon exposure. The resist containing CpDP-Tf gave the higher resolution comparing with that containing triphenylsulfonium trifluoromethanesulfonate

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1. Introduction

In a chemically amplified resist system[1], photoacid generators (PAGs) generate acid upon irradiation, and this acid catalyzes chemical reactions. Triphenylsulfonium salts[2], widely being used, absorb so much light at 193 nm that a considerable amount of the light is absorbed by the upper part of the resist film. Because of this phenomenon, most of the light cannot reach the bottom of the resist, and the resist is not dissolved clearly as approaching to the resolution limit. Much effort has been devoted to the development of transparent matrix resins[3] rather than transparent PAGs. There were some trials to adapt the photobleaching effect to deep UV resist systems, but they didn't work well because of the nature of PAGs such as thermal stability, solubility and contrast[4]. It has been recognized for many years that there exist numerous similarities in the reaction of unsaturated olefins and simple cyclopropane[5]. The absorbance of cyclopropyl group[6] is just a little smaller than that of phenyl group. In this paper, the cyclopropyl group was introduced into the PAG in order to reduce absorbance at 193 nm upon irradiation.

2. Experimental

2.1. Materials

Silver trifluoromethanesulfonate, diphenyl sulfide, 1-chloro-3-iodopropane, t-butyl methacrylate, sodium hydride, sodium trifluoromethanesulfonate, trifluoromethanesulfonic acid, and cyclohexanone were purchased from Aldrich chemical company and used without purification. Poly(t-butyl methacrylate) was synthesized using 1 mol % 2,2'-azobisisobutyronitrile (AIBN) as an initiator in 1,4-dioxane at 60 °C under vacuum in a sealed ampoule for 12 hr. Triphenylsulfonium trifluoromethanesulfonate (TPS-Tf) was purchased from Midori Kagaku Co., Ltd. Cyclopropyldiphenylsulfonium trifluoromethanesulfonate (CpDP-Tf) was synthesized following the previously reported procedures[7]. The matrix polymer, SAS4.1 was provided by Samsung Electronic Co., Ltd.

2.2. Methods

2.2.1. Basic Measurement

The synthetic compounds were confirmed by proton, carbon, and fluorine NMR spectral data. Thermogravimetric analysis (TGA) was obtained on a Perkin-Elmer TA 7 series thermal system. The

TGA measurement was taken at a heating rate of 10 °C /min under nitrogen.

2.2.2. UV absorbance

Matrix Polymer. UV Spectra were recorded as spincoated films on quartz plates with a Hewlett-Packard Model 8453 spectrophotometer. A resist solution was prepared by dissolving 0.2 g of poly(*t*-butyl methacrylate) (P(TBMA)) in cyclohexanone. This solution was filtered through a 0.2 µm filter and spin-coated onto quartz plates. The UV absorbances before and after exposure were observed.

Resist film. Resist solutions were prepared by dissolving 0.2 g of P(TBMA) and 0.01 g of TPS-Tf (5 wt%) or 0.01g of CpDP-Tf in cyclohexanone. These solutions were also filtered through a 0.2 µm filter and spin-coated onto quartz plates. The UV absorbances before and after exposure were observed. The data were corrected by subtracting the absorbances of P(TBMA) before and after exposure from the observed data.

Bleaching Test. A resist solution was prepared by dissolving 0.2 g of PTBMA and 0.02 g of CpDP-Tf in cyclohexanone. This solution was filtered through a 0.2 µm filter and spin-coated onto quartz plates. UV absorbance differences between before and after exposure were measured as increasing the amount of exposing dose. The data were corrected by subtracting the difference of absorbance of P(TBMA) from the observed data.

2.2.3. Lithographic evaluation

Two kinds of resists were formulated by dissolving SAS4.1[8] (Figure 1) and TPS-Tf (1 wt%) or CpDP-Tf (0.9 wt%) in propylene glycol monomethyl ether acetate (PGMEA) and then the solutions were filtered with a 0.2 µm teflon membrane filter. Resist solutions were coated to yield 0.35 µm-thick films on substrates and soft-baked at 120 °C for 90 sec. 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 sec on a hot-plate and developed in a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution for 60 sec.

Figure 1. SAS4.1

3. Results and Discussion

3.1. Thermal stability

The TGA thermogram shows that the onset decomposition temperature is 165 °C.

3.2. UV absorbance

The absorbance of CpDP-Tf is somewhat smaller than that of TPS-Tf at 193 nm because the phenyl group absorbs more than the cyclopropyl group. The absorbance of CpDP-Tf decreases upon exposure while that of TPS-Tf rarely changes. Fig. 2 shows the comparison of UV absorbance of two PAGs.

Figure 2. Change in absorbance (µm) spectra of the resist films containing a) TPS-Tf and b) CpDP-Tf, before and after UV irradiation.

The absorbance differences between before and after exposure of 10 wt% CpDP-Tf in the P(TBMA) solution were measured. For the exact data, we compensated the absorbance of P(TBMA) from measured data. Bleaching effect[9] increases as the exposing dose is increased. Figure 3 shows the experimental results.

Figure 3. Δ Absorbance(μm) vs Exposing dose (mJ)

From the results of UV absorbance change, we can suggest the plausible mechanism of the onium salt bearing a cyclopropyl group in the structure. The results are shown in Scheme 1.

Scheme 1. Plausible mechanism of the PAG with a cyclopropyl group.

3.4. Lithographic evaluation

The comparison experiment was proceeded between two kinds of PAGs. All of the conditions were the same. The different wt% was used to make the equal mol% (TPS-Tf (1 wt%), CpDP-Tf (0.9 wt%)). Each photoresist was optimized under the same condition (prebake, post-exposure bake, post-exposure delay time, develop time and so on). SEM images of the results are shown in Figure 4. The resist with TPS-Tf already has shown the 0.13 μm line and space pattern at the previous papers[8]. There are two distinguishing differences. The one is that the side-wall shape of the CpDP-Tf-containing resist is relatively rectangular and the edge of TPS-Tf-containing resist is slightly sloped. Generally, the resists containing TPS-Tf show a somewhat tapered pattern because of the strong absorption[10]. The other is that at the pattern of 0.12 μm which is up to now the resolution limit by using the conventional exposing method, there is some scum in the TPS-Tf-containing resist, but there is a great improvement in the shape for the CpDP-Tf-containing resist. In the case of TPS-Tf, even if we may increase the

dose of exposure, or develop for a longer time, the scum does not disappear. The main reason of this difference between the two is probably related to the bleaching effect of PAGs. In the case of TPS-Tf, a great amount of light is absorbed by the upper part of the resist film. As a result, the light cannot reach the bottom of the resist and it makes scum at the resolution limit. But in the case of CpDP-Tf, after the light is exposed, PAGs turn to be more transparent, and this makes the light go through to the bottom, and the exposed region dissolved clearly at the bottom of the resist.

Figure 4. SEM images of the two resists: a) with TPS-Tf b) with CpDP-Tf.

4. Conclusion

A PAG bearing a cyclopropyl group which can make the PAG photobleachable was synthesized. The decrease of UV absorbance of the PAG was observed upon irradiation. And actually we can certify the bleaching effect in the evaluation of the photoresist by the comparison experiment with TPS-Tf which is widely used because of its good thermal stability and especially good performance. When using CpDP-Tf which shows the photobleaching effect, the higher resolution was obtained comparing with the non-bleaching PAG, TPS-Tf.

5. Acknowledgements

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6. References

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