Onium Salt Type Photoacid Generator Containing Tetrakis(pentafluorophenyl)borate

JongSoo Lee, Nobukazu Miyagawa, Shigeru Takahara and Tsuguo Yamaoka

Department of Information and Image Sciences, Faculty of Engineering, Chiba University, Chiba 263-8522, Japan

Keywords: tetrakis(pentafluorophenyl)borate, photoacid generator, acid diffusion, quantum yield, thermal stability

1. Introduction
Chemically amplified resists based on acid catalyzed reaction have been widely utilized in the development of highly sensitive resists. Photoacid generator (PAG) that generated acids upon irradiation with light played an important role on the progress of chemically amplified resist. Some of cationic polymerization initiators were applied as a PAG in photolithography. Representative cationic polymerization initiators are diphenyliodonium salt, triphenylsulfonium salt, iron arene complex, nitrobenzyl sulfonate and so on. [1-6] Especially, onium salts have been explored and utilized as a PAG.

Onium salts as a photoacid generator have several advantages such as thermal stability and easy structure modification to alter their spectral absorption characteristics. On the other hand, they have low solubility in common organic solvents.

In this study, we investigate that new type PAG containing tetrakis(pentafluorophenyl)borate as an anion part can be apply to photolithography.

2. Experimental
2.1. Materials
Two kinds of new photoacid generators were examined in this study are 4-cumeny1-4'-tolylidonium tetrakis(pentafluorophenyl)borate (FX-TePBI), triaryl sulfonium tetrakis(pentafluorophenyl)borate (FX-TePBS) (Fig. 1). Cation part of FX-TePBS was mixed triphenyl sulfonium derivatives. There were provided from Nippon Shokubai Co. Triphenyl sulfonium trifluoromethane sulfonate (TPS-OTf) and diphenyliodonium trifluoromethane sulfonate (DPI-OTf) were chosen for the comparative evaluation as a PAG. These onium salts were obtained from Midori Chemical Co. These PAGs have similar structure such as triphenylsulfonium and diphenyliodonium in cation part of new type PAGs and were generally used as a PAG for ArF and KrF lithography.

2.2. UV Measurement in Solution and Films
Acetonitrile has high transparency in the short wavelength region was used as a solvent for UV spectrum. Quartz cell for solution and quartz plate for the film were used respectively. In the case of the film, photopolymer solution having poly(methyl methacrylate) (PMMA) as a base polymer was spin-coated to obtain about 1 µm thick film and dried in vacuo. Spectral changes of the film were followed after irradiation with a low pressure mercury lamp.

Received October 13, 2000
Accepted November 24, 2000
2.3. Quantum Yield of Acid Generation in solution

The acetonitrile solution of PAG (2×10⁻³ mol/dm³) in a quartz cell was irradiated at 254 nm with a low pressure mercury lamp. After irradiation, 1 ml of the solution was mixed with 3 ml of 5.2×10⁻⁵ mol/dm³ acetonitrile solution of sodium salt of tetrabromophenol blue (TBPB) and the absorption spectrum of the mixture was measured. Changes of absorption spectra of TBPB at 618 nm were compared. [7-9]

2.4. Measurement of Acid Diffusion

At first, an under layer was spin-coated onto Si-wafer and followed by baked at 130°C for 30 min. Then an upper layer was spin-coated on the under layer and baked at 120°C for 10 min. After irradiation this film was baked in various temperatures for 5 min and was developed in 2.38 wt% tetramethylammonium hydroxide (TMAH) for 1 min. Value of acid diffusion was determined from difference in film thickness between exposed area and unexposed area. The film thickness was measured with profiler (Tencor Alphastep 200).

2.5. Lithographic Evaluation

Poly (methyl methacrylate-co-methacrylic acid-co-t-butyl methacrylate) [poly(MMA₆₅.₅-co-MAA₁₄.₇-co-tBuMA₁₉.₇)] was prepared according to the literature. [10] Photopolymer solutions containing 2.6 mol% PAG against the polymer were spin-coated on Si-wafer to give a 1 µm thick film. The films were pre-baked (PB) at 120°C for 10 min and exposed with the low pressure mercury lamp. Post exposure bake (PEB) was carried out at 130°C for 5 min. They were developed in a 0.1 wt% TMAH solution.

3. Results and Discussion

3.1. Behavior of PAG in Film

Spectral changes of PAGs in film after photo-irradiation are shown in Fig. 2 and Fig. 3 (PAG contained 5 wt% against the polymer). An absorption band of FX-TePBI increased at around 230 nm and decreased at around 250 nm and isosbestic point appeared at 235 and 261 nm. Spectral change of FX-TePBS was also very similar to those of FX-TePBI. A new absorption band at 260 nm increased and that at 300 nm decreased with photo-irradiation. Isosbestic points at 241 and 297 nm were observed. Spectral changes in films were similar to those in solution.

From the result it was confirmed that photodecomposition of the PAGs in film as well as in solution proceeded.

3.2. Solubility in Organic Solvents and Thermal stability

The solubility of PAG is one of important factors for lithography. General organic solvents such as cyclohexanone, diethylene glycol dimethyl ether, ethyl lactone, and propylene glycol monoethyl ether acetate were used in lithography process. These new PAGs showed good solubility in all of solvents. Their solubility in diethylene glycol dimethyl ether was described in Table 1. It is deduced that an increase in the solubility is due to fluorine of pentafluorophenyl group in the anion part.

Another important factor is thermal stability in baking steps such as PB and PEB. Decompose temperature of PAGs were measured by TG/DTA
with a rate of 5°C/min. Both PAGs possess high thermal stability up 200°C. On the basis of these results, it is thought that PAGs have adequate property as a PAG.

Table 1. Characteristics of Photoacid Generators

<table>
<thead>
<tr>
<th>PAG</th>
<th>extinction a)</th>
<th>Sol b)</th>
<th>Tm(C) c)</th>
<th>Td(C) c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FX-TePBI</td>
<td>1.48×10^4</td>
<td>70.6</td>
<td>134</td>
<td>226</td>
</tr>
<tr>
<td>FX-TePBS</td>
<td>1.50×10^4</td>
<td>65.4</td>
<td>167</td>
<td>315</td>
</tr>
<tr>
<td>DPI-OTf</td>
<td>6.28×10^3</td>
<td>8.7</td>
<td>178</td>
<td>181</td>
</tr>
<tr>
<td>TPS-OTf</td>
<td>1.31×10^4</td>
<td>15.4</td>
<td>136</td>
<td>357</td>
</tr>
</tbody>
</table>

a) molar extinction coefficient in acetonitrile (1×10^3 mol/dm^3)

3.3. Quantum Yield of Acid Generation

The acid generation yield was measured using TBPB as an acid indicator. Absorption band of TBPB at around 620 nm was changed by the addition of an acid quantitatively. Absorption changes of TBPB using p-toluenesulfonic acid as a standard material were calibrated.

In the chemically amplified resist, PAGs play an important role on its sensitivity. Quantum yield of PAG is directly related to sensitivity. The results that determined from absorption changes at 618 nm due to acid generation were shown in Fig. 4. Quantum yields of acid generator of FX-TePBI and FX-TePBS were 0.0224 and 0.0222, respectively. These values have little difference in comparison with that of recent representative PAGs.

3.4. Comparison of Acid Diffusion

Acid diffusion in baking step is a key step for high resolution. Many methods to measure the rate of acid diffusion were developed. [11-13] In this study, acid diffusion was measured using bi-layers which consist of an upper layer includes poly-(p-hydroxystyrene) (PHS) and PAG and an under layer contains PHS and vinyl ether crosslinker. During PB, an under layer was crosslinked between hydroxy group of PHS and vinyl group of crosslinker. [14] The upper layer with various PAG on the layer was spin-coated. Acid generated from PAG was diffused to under layer. Then the layer was decrosslinked and was dissolved in developer. PAGs having tetrakis(pentafluorophenyl)borate were expected to have low diffusion rate because it is inverse proportion to an anion size. It is appears from the result in Fig. 5 that diffusion rate of acid generated from PAG with tetrakis (pentafluorophenyl)borate was lower than that of PAG with trifluoromethane. We assumed that the inversion of film thickness in the presence of DPI-OTf and TPS-OTf at 80-90°C due to their swelling in the development.

3.5. Application to Photolithography

The evaluation of these PAGs in the photolithography was carried out by the use of polymer bearing t-butyl protecting groups. This is a positive working resist which shows solubility change due to deprotection by irradiation and subsequent bake. As shown in Fig. 6 PAGs have sufficient sensitivity for application to lithography.

4. Conclusion

Novel onium salts were used as a PAG in photolithography. The new PAGs involve tetrakis(pentafluorophenyl)borate as an anion part.
These have high solubility in organic solvents due to fluorine and asymmetric cation part and good thermal stability and sufficient sensitivity. Moreover, low diffusion rate of acid due to relatively large size of an anion was proved. These PAGs are useful to improvement of resolution.

Acknowledgement

We would like to express our thanks to Mr. Y. Asako and Mr. H. Mitsui of Nippon Shokubai Co. for their support and advice.

References