Optimization of photoacid generator in CA resist for EUVL

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\textbf{ABSTRACT}

We succeed in developing beneficial photoacid generator (PAG) for EUV exposure. In a high annealing type resist system in which poly-hydroxystyrene employed as a base resin, we found that sulfonium salts which employed cyclo(1,3-perfluoropropanedisulfone) imidate employed as an anion of PAG is more sensitive than perfluorobutanesulfonate employed as an anion of PAG under extreme ultraviolet (EUV) exposure. However, the sensitivities were different under EUV and electron beam (EB) exposures. It indicates that the distinctive acid production reaction is occurred under EUV exposure in comparing under EB exposure. As results of the time dependency mass spectroscopy and the Fourier Transform Infrared Spectroscopy (FT-IR), EUV induced reaction of cyclo(1,3-perfluoropropanedisulfone) imidate employed as an anion of PAG occurred more efficiently than that of perfluorobutanesulfonate employed as an anion of PAG.

\textbf{KEYWORDS : EUVL, high sensitivity, chemically amplified resist, onium salts}

\textbf{1. INTRODUCTIONS}

Extreme ultraviolet lithography (EUVL)\textsuperscript{1) is now planned to address the 32 nm node technology below. The lithographic performances of a variety of resist types have been previously evaluated\textsuperscript{2-7) including chemistries of both chemically amplified resist\textsuperscript{8-15) and non-chemically amplified resist in EUVL\textsuperscript{8, 10, 11) However, at the industrial stand point, the current EUV resist is not yet mature enough to achieve some of the required characteristics, such as line edge roughness (LER), sensitivity and outgassing. The LER target is reduced to 1.5 nm (3σ) to maintain the device performance. Since the required LER specification size is as same as a size of resist molecule, this target itself is challenging. Furthermore, it is especially challenging when combined with a sensitivity target of 2–5 mJ/cm\textsuperscript{2}.\textsuperscript{16)} Since, the wavelength using for EUVL is about 1/20 shorter than that using for conventional optical lithography, shot noise in EUV exposure influences LER controllability. Therefore, the photochemical reaction efficiency of a resist has to be increase under EUV exposure. Focusing on CA resist, the acid generation efficiency has to increase under EUV exposure to satisfy the specification of LER.

There are also few reports to improve sensitivities of resist materials.\textsuperscript{17, 18)} We reported that the resist using a sulfonium salt on the basis of a new photo-acid-generator (PAG) could achieve higher $E_0$ sensitivity in comparison with a conventional PAG under EUV exposure.\textsuperscript{19)} The same trend was not observed with other light sources such as electron-beam (EB) and 248 nm exposures. This indicates that there is a distinctive photoysis process occurring in the resist film matrix under EUV exposure.
This paper focused on a beneficial photoacid generator for EUV exposure. Furthermore, we will discuss the chemical reaction differences for a onium salts under EUV exposure.

2. EXPERIMENTS

2.1. Experimental setup

The outgas experiment was carried out at the BL3 beamline of NewSUBARU synchrotron radiation (SR) facility. The SR source for this beamline is a bending magnet of the NewSUBARU storage ring. The storage ring operates at an electron energy of 1.0 GeV. The experimental setup is shown in Figure 1. The resist evaluation system simulating a six-mirror optics was utilized. SR light wavelength was mono-chromated to 13.5 nm by being reflected seven times by Mo/Si multilayer.

The outgassing species collected from the resist during the EUV exposure was analyzed with HAL511/3L quadrupole mass spectrometer (Hiden Analytical Ltd.) connected to the resist evaluation chamber. The distance between the resist sample and the detector is maintained approximately at 30 mm to increase the detection efficiency of the outgassing ion species. The atmospheric pressure in the resist test chamber is maintained at less than \(3.0 \times 10^{-5}\) Pa.

![Fig. 1 EUV resist evaluation system.](image)

2.2. Resist samples and process conditions

The samples were formulated with a polymer, a solvent and 10wt% onium salt employed as a PAG (against the base polymer). We employed poly(hydroxystyrene-co-t-butylacrylate) as a base polymer. Two different types of triphenylsulfonium derivative PAGs were evaluated. Resists A and B employ triphenylsulfonium cyclo(1,3-perfluoropropanedisulfone) imidate (TPS-IMIDATE) and triphenylsulfonium perfluorobutanesulfonate (TPS-PFBS) as PAGs, respectively. Two different types of 4-(tert-butyl)phenyliodonium derivative PAGs were evaluated. Resists C and D employ bis-4-(tert-butyl)phenyliodonium cyclo(1,3-perfluoropropanedisulfone) imidate (BPI-IMIDATE) and bis-4-(tert-butyl)phenyliodonium perfluorobutanesulfonate (BPI-PFBS) as PAGs, respectively. Propyleneglycol monomethyletheracetate (PGMEA) was employed as a solvent. The detail of resist sample formulations and structure are shown in Table 1.

The sample films were spin-coated on a silicon wafer and were baked on a hot plate at 130°C for 90 s. The film thickness was fixed at 100 nm for all samples and determined by using a multi-wavelength interference thickness measurement tool Nanospec model 6100A manufactured by NANOmetrics Co. Ltd. After exposure, post exposure bake (PEB) conditions are carried out at 110°C for 90 s. The puddle development was performed with NMD-3 at 23°C for 60 s, which was mainly containing of 2.38% tetra-methylammonium hydroxide (TMAH) aqueous solution. The rinse was performed with deionized...
water at 23˚C for 60 s. After the rinse, the remaining thickness was measured to obtain the sensitivity curve.

Table 1. Resist samples employed in the experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resist A</th>
<th>Resist B</th>
<th>Resist C</th>
<th>Resist D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>![Resin Image]</td>
<td>![Resin Image]</td>
<td>![Resin Image]</td>
<td>![Resin Image]</td>
</tr>
<tr>
<td>PAG</td>
<td>![PAG Image]</td>
<td>![PAG Image]</td>
<td>![PAG Image]</td>
<td>![PAG Image]</td>
</tr>
<tr>
<td>Solvent</td>
<td>propylene glycol monomethylether acetate (PGMEA)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. Sensitivity under EUV exposure

The sensitivity curves of resists A, B, C and D are shown in Figure 2. E₀ sensitivity is defined as a threshold dose to completely develop. E₀ sensitivities of resists A, B, C, and D are 1.1 mJ/cm², 3.8 mJ/cm², 2.0 mJ/cm², and 4.0 mJ/cm², respectively.

In comparing resists A and B, the sensitivity of resist A is four times higher sensitive than that of resist B. Both resist A and B employ triphenylsulfonium (TPS) as a cation of PAG. The different points were only an anion structure. Resists A and B employ cyclo(1,3-perfluoropropanedisulfone) imidate (IMIDATE) and perfluorobutanesulfonate (PFBS) as anions of PAG, respectively.

Furthermore, in comparing resists C and D, the sensitivity of resist C is twice higher sensitive than that of resist D. Both resist C and D employ bis-4-(tert-butyl)phenylidonium (BPI) as a cation of PAG. The different points were only an anion structure. Resists C and D employ IMIDATE and PFBS as anions of PAGs, respectively.

As results, IMIDATE employed as an anion of PAG is more sensitive than PFBS employed as an anion of PAG under EUV exposure.

Since an E₀ sensitivity tendency in iodonium salts shows slightly weaker than that in sulfonium salts, it is considered that these slight differences of sensitivities caused by an inhibition effect of iodonium salts under EUV exposure.

3.2. Comparison of sensitivities under EUV and EB exposures

E₀ sensitivity measurements of resists A and B were carried out under EB exposure to compare E₀ obtained under EUV exposure. EB exposure was carried out by using an electron beam direct writing tool with an accelerated voltage of 70 kV. Resist thickness was 150 nm and resist components and process were the same as using under EUV exposure. Tables 2 and 3 show E₀ sensitivities of resists A, B, C and D under EUV and EB, respectively. As a result, E₀ sensitivities of resists A and B under EB exposure are almost the same. Furthermore, E₀ sensitivity of resist C and B under EN exposure are almost same.
However, $E_0$ sensitivity of resist A is higher than that of resist B under EUV exposure. Furthermore, $E_0$ sensitivity of resist C is twice higher than that of resist D under EUV exposure. It is confirmed that a selection of an anion of PAG for EUV exposure is much more effective to achieve a high acid generation yield but for EB exposure.

![Sensitivity curve of resists A, B, C and D](image)

**Table 2. Resist sensitivity under EUV exposure**

<table>
<thead>
<tr>
<th>Resist</th>
<th>$E_0$ (mJ/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist A</td>
<td>1.1</td>
</tr>
<tr>
<td>Resist B</td>
<td>3.8</td>
</tr>
<tr>
<td>Resist C</td>
<td>2.0</td>
</tr>
<tr>
<td>Resist D</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Table 3. Resist sensitivity under EB exposure**

<table>
<thead>
<tr>
<th>Resist</th>
<th>$E_0$ (µC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist A</td>
<td>14.3</td>
</tr>
<tr>
<td>Resist B</td>
<td>14.6</td>
</tr>
<tr>
<td>Resist C</td>
<td>14.0</td>
</tr>
<tr>
<td>Resist D</td>
<td>15.0</td>
</tr>
</tbody>
</table>

### 3.3. Reaction of PAG under EUV exposure

#### 3.3.1. FT-IR measurements

FT-IR-spectra were measured to study the decomposed mechanisms of resists A and B. The spectra were measured to compare the cases before EUV exposure and after EUV exposure for resists A and B. The FT-IR spectra before and after the exposures of resists A is shown in Fig. 3. For resist B, the absorbance peaks of the spectra did not show any significant change before and after exposures. However, there is an absorbance peak change at approximately 1156 cm$^{-1}$ in resist A. FT-IR spectra of PAG of resists A is shown in Fig. 4. The peak at approximately 1156 cm$^{-1}$ in Fig. 3 corresponds to a sulfonic acid. As a result, the outgassing measurements and the FT-IR spectra measurements show that the EUV-induced reaction of TPS-IMIDATE occurred more efficiently than that of TPS-PFBS. It is considered that since the IMIDATE employed as the anion of PAG decomposed under EUV exposure to produce a larger amount of acid than PFBS did, the large amount of sulfonic acid is induced by the photodecomposition reaction of IMIDATE. Therefore, IMIDATE which is employed as the anion of PAG, achieves the fast photospeed characteristics under EUV exposure.

#### 3.3.2. Outgassing ion species of PAG

The outgassing characteristics is measured to better understand the detailed mechanism for obtaining a high sensitivity.

The outgassing species collected from the resist during the EUV exposure was analyzed with HAL511/3L quadruple mass spectrometer (HIDEN Co., Ltd) connected to the resist test chamber. The distance between the resist sample and the detector is approximately 30 mm. The atmospheric pressure in the resist test chamber is maintained at less than $3.0 \times 10^{-5}$ Pa. In order to avoid any potential contamination of the sample through outgassing of the filament in the mass spectrometer, the resist sample was moved into the chamber 600 seconds prior to starting the outgas measurement.

The transient mass spectra measurement time for each resist sample was a total of 189 seconds, the first 63
seconds is for background measurement. EUV light is then irradiated to measure outgassing by mass spectrometer for 63 seconds. The last 63 seconds is for background re-measurement. (23.9 mJ/cm²).

However, the content of PAG is almost 10 wt% for the base polymer. Thus the outgassing species from PAG is very weak. Therefore, to increase the signal noise ratio of the ion counts of the outgassing species from PAG, the integrated ion counts over the exposure time is calculated based on the measurement results of the time dependency of ion counts. Figs. 5, 6, and 8 show time dependency of ion counts for resists A, B, and C, respectively.

![Fig. 3 FT-IR spectra of resist A before and after exposure](image)

![A](image)

**Fig. 3** FT-IR spectra of resist A before and after exposure

![A](image)

**Fig. 4** FT-IR spectra of PAGs of resists A
As a result of outgassing measurement of resist A, outgassing species of mass numbers of 64, 80, 128, 142, 150 are observed as the photodecomposition species from PAG. For resist B, outgassing species of mass number of 64 and 80 are observed as the photodecomposition species from PAG. As shown in Fig. 7, the integrated ion counts over 60 s exposure for each outgassing species which have mass number of are obtained by integrating ion counts over 60 s. The outgassing species which has mass number of 64, 80, 128, 142 are assigned as SO₂, SO₃, CF₂SO₂N, and SO₂NO₂S, respectively. Furthermore, for resist B, outgassing species of mass numbers of 63 and 64 are observed as the photodecomposition species from PAG. Since the ion counts are very small for other species from TPS-PFBS, the ion counts are too small to integrate over 60 s. The outgassing species which has mass number of 64, 80 are assigned as SO₂, SO₃, respectively.

Fig. 5 Outgassing measurement result of resist A.

Fig. 6 Outgassing measurement result of resist B.
Resist A contains PAG anion of imidate derivatives, which carried out photodecomposition reaction of PAG anion under EUV exposure. This reaction will be expected to generate many acidic species, which has the potential of becoming a catalyst for the de-protecting reaction. This mechanism is useful for a resist design to obtain a high sensitivity EUV resist comparison with resist B.

Figure 8 shows the time dependency of the outgassing species from resist C. The measured outgassing species of mass numbers are shown in Table 4. Large amount of inspecting species was observed at less than m/z 80. There is a possibility of solvent, PAG decomposition and de-protect species induced outgassing and fragmentation from large mass number compounds. As a result, estimated many fragment species of decomposed PAG anions were observed from resist C. Large amount of m/z 64, which related SO₂ was observed. It is confirmed that IMIDATE employed as an anion of PAG, which carried out distinctive photodecomposition reactions under EUV exposure. Thus these reactions can induce the higher sensitivity in resist C than resist D.

As results of the time dependency mass spectroscopy and the FT-IR spectroscopy, the distinctive photodecomposition reactions of IMIDATE of an anion of PAG will be expected to generate many acidic species, which has the potential of becoming a catalyst for a de-protecting reaction. This mechanism is very useful for the resist design to develop a high sensitivity EUV resist for EUVL.

Table 4. Measurement mass numbers and estimated outgassing fragment species.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Estimated outgassing species</th>
<th>Source</th>
<th>m/z</th>
<th>Estimated outgassing species</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>CH₃O⁻</td>
<td>Solvent</td>
<td>80</td>
<td>SO₂</td>
<td>PAG</td>
</tr>
<tr>
<td>43</td>
<td>CH₃CO⁻</td>
<td>Solvent</td>
<td>94</td>
<td>C₆H₅OH</td>
<td>Polymer</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
<td>All</td>
<td>126,127</td>
<td>I</td>
<td>PAG</td>
</tr>
<tr>
<td>56</td>
<td>CH₂=CH(CH₃)₂</td>
<td>Polymer</td>
<td>128</td>
<td>NSO₂CF₂</td>
<td>PAG</td>
</tr>
<tr>
<td>57</td>
<td>(CH₃)₂C</td>
<td>Polymer</td>
<td>134</td>
<td>(CH₃)₂CPhH</td>
<td>PAG</td>
</tr>
<tr>
<td>64</td>
<td>SO₂</td>
<td>PAG</td>
<td>150</td>
<td>(CF₂)₃</td>
<td>PAG</td>
</tr>
<tr>
<td>78</td>
<td>C₆H₆</td>
<td>PAG</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
4. CONCLUSIONS

In a high annealing type resist system in which poly-hydroxystyrene employed as a base resin, we found that onium salts which employed cyclo(1,3-perfluoropropanedisulfone) imidate as an anion of PAG are more sensitive rather than those which employed perfluorobutanesulfonate as a anion of PAG under EUV exposure. However, the sensitivities were different between under EUV and EB exposures. It is confirmed that the distinctive acid production reaction is occurred under EUV exposure in comparing EB exposures. As results of the time dependency mass spectroscopy and the FT-IR spectroscopy, the distinctive photolysis reactions of IMIADTE of an anion of PAG will be expected to generate many acidic species, which has the potential of becoming a catalyst for a de-protecting reaction. It is confirmed that the EUV-induced reaction of IMIDATE employed as an anion of PAG occurred more efficiently than that of perfluorobutanesulfonate employed as an anion of PAG. Therefore, IMIDATE which is employed as an anion of PAG achieves the high sensitivity under EUV exposure. As results, we succeed in developing high sensitivity chemically amplified resist components which has to meet requirement of LER and a sensitivity less than 5.0 mJ/cm².

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REFERENCES