Lithographic Evaluation of Chemically Amplified Molecular Resist for below 22nm Resolution

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Molecular resist material having only one protecting group per molecule (Prot-1) was designed and synthesized. After confirming the structure and purity of Prot-1, Resist-A formulated with Prot-1 as a base material was prepared. Resist-A showed good contrast curve. To confirm the decomposition behavior, Resist-A was analyzed by using High Performance Liquid Chromatography (HPLC) at the exposure dose of E0 value exposed by electron beam (EB). From the HPLC analysis, it was found that the dissolution contrast of Resist-A was caused by deprotection reaction of Prot-1. We evaluated resolution limit of Resist-A by using EB. Resist-A showed 25 nm hp resolution and partially resolving 20 nm at the exposure dose of 36 μC/cm². The mechanism which generates dissolution contrast by the reaction of just one protecting group per molecule would be a key of 22 nm generation and beyond at the point of the high resolution property.

Keyword: chemically amplified positive tone, Electron beam lithography, molecular resist, decomposition analysis

1. Introduction

In order to meet the growing demands of the semiconductor industry, process techniques and resist materials have been developed. Extreme ultraviolet (EUV) and electron beam (EB) lithography are emerging next generation technologies for pattern fabrication of 22 nm and beyond. For 22 nm node, high resolution and low line width roughness property are needed simultaneously 1). Non-chemically amplified positive- and negative-tone resists are reported using TsOTP and ASITPA, respectively 2). Recently, many researchers intensively reported about molecular resist materials to improve line width roughness (LWR) and resolution because of their smaller size than that of polymeric materials 3-5). Molecular resist showed smaller surface roughness than polymeric material 6). For LWR reduction point of view, it is reported that controlling protecting group distribution of molecular resist material is an effective method, which leads to controlling chemically amplified (CA) reaction in resist film 7-10). It is also reported that low molecular weight material of polymer showed good resolution and LWR 11).

In this paper, we prepare and evaluate molecular resist material, which has only one protecting group per molecule for dissolution contrast (Prot-1). We discuss about resolution limit of Prot-1 for targeting 22 nm node.
2. Experimental

2.1. Materials and analyses

$^1$H Nuclear Magnetic Resonance (NMR) spectra were obtained using deuterated dimethyl sulfoxide (DMSO-<sub>d6</sub>) solvent with tetramethylsilane (TMS) acting as an internal standard using a JEOL AL-400 (400 MHz) spectrometer. Infrared (IR) spectra were recorded using a Perkin-Elmer 2000 spectrometer. Decomposition analysis was carried out using a high-performance liquid chromatography (HPLC) analyzer (Shimadzu Corporation, SCL-10AVP).

2.1.1. Synthesis of CA-1

1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (7.0 g, 37 mmol) salt, 1-hydroxymethyl adamantane (5.0 g, 30 mmol) and carboxylic acid derivative of CA-2 (27.6 g, 33 mmol) were dissolved in dry tetrahydrofuran (300 mL) under an atmosphere of nitrogen. After forming a clear solution, dimethylaminopyridine (DMAP, 0.12 g, 1.0 mmol) was added to a solution at the temperature of 0 °C. After stirring for 10 h, the reaction was quenched with water. The mixture was concentrated and ethyl acetate was added. The mixture was extracted using ethyl acetate three times. Finally, a yellow powder of CA-1 was obtained after drying in vacuo (2.3 g, yield: 40%). The purity of the product was 99.0% analyzed by HPLC. The chemical structure is shown in Fig. 1. IR: 3386 (COOH), 2905 (CH), 2850 (CH), 1737 (C=O) and 1285 cm<sup>-1</sup> (Ar); $^1$H-NMR δ 8.85 s 4H, 6.32-6.78 m 14H, 5.82 d 2H, 4.62 s 4H, 4.46 s 2H, 3.71 s 2H, 3.57 s 2H, 1.98 s 12H, 1.89 s 3H, 1.85 s 12H, 1.43-1.66 m 12H.

2.1.2 Synthesis of Prot-1

CA-1 (2.2 g, 2.3 mmol) and 2-methyl-2-adamantyl bromoacetate (0.72 g, 2.5 mmol) were dissolved in dry tetrahydrofuran (20 mL) in a nitrogen atmosphere. After forming a clear solution, triethyl amine (0.40 g, 4.0 mmol) was added dropwise, and a white precipitate gradually formed. After stirring for 10 h, the reaction was quenched with water. The mixture was concentrated and ethyl acetate was added. The mixture was extracted using ethyl acetate three times. Finally, a yellow powder of Prot-1 was obtained after drying in vacuo (2.3 g, yield: 85%).

2.2 Resist sample preparation

To evaluate lithographic property, resist samples formulated with Prot-1, a photo acid generator (PAG), a quencher, and a casting solvent were prepared. Triphenylsulphonium perfluoro-1-butenesulfonate (TPS-PFBS) and trioctylamine (TOA) were used as the PAG and quencher, respectively. The casting solvent was a mixture of propylene glycol monomethylether acetate (PGMEA) and propylene glycol monomethylether (PGME). The details of the resist formulations are described in Table 1.

![Figure 2. Synthesis of Prot-1](image)

Table 1. Resist sample formulation

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Material</th>
<th>PAG</th>
<th>quencher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist-A</td>
<td>Prot-1</td>
<td>TPS-C4</td>
<td>Trioclyamine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10wt%</td>
<td>1wt%</td>
</tr>
</tbody>
</table>

2.3 Decomposition analysis of resist-A

The sample of resist-A was spin-coated on silicon wafers and heated on a hot plate at 110 °C for 90 s. The film thickness of resist-A was measured using a multiwavelength interference thickness measurement tool (Nanospec model 6100A). The EB exposure was carried out using a Hitachi HL-800D EB direct writing tool with an acceleration voltage of 70 kV connected to a...
coater/developer in-line system. After EB exposure dose of $E_0$ value and post exposure bake (PEB), a resist film was scratched out and analyzed by HPLC.

2.4 Lithographic evaluations
To investigate the lithographic performance of molecular resist, EB lithographic evaluation was carried out by 50 kV of EB writing system (Elionix Inc.) connected to a coater/developer in-line system. The sample films were spin-coated on silicon wafers and baked on a hot plate at 110°C for 90 s. Following the EB exposure, the resist films were baked at 90°C for 90 s for post-exposure bake (PEB) and developed in NMD-3 2.38 wt% (Tokyo Ohka Kogyo) aqueous 0.26 N tetramethylammonium hydroxide (TMAH) at 23°C. The dose of $E_{size}$ was determined to be optimum dose when the feature size of 50 nm (lines/spaces=1/1) was achieved. The top-view of the patterns fabricated was observed with a scanning electron microscope (SEM), Hitachi S-9220.

Results and Discussion
3.1. $^1$H-NMR analysis of CA-1
CA-1 was synthesized as that described in section 2.1.1. Figure 3 shows characteristic parts of $^1$H-NMR spectra of CA-1 and CA-2, respectively. The peaks in CA-1 assigned to $H^a$ and $H^b$ were observed separately while the peak in CA-2 derived from $H^e$ was observed as a single peak. The peaks in CA-1 derived from $H^f$ and $H^g$ were also derived separately while the peak in CA-2 derived from $H^f$ was observed as a single peak. These results show that chemical structure of CA-1 is asymmetric, that is, esterification is occurred at just one site of two carboxylic groups in one molecule remaining one carboxylic group in CA-1. Furthermore, a peak of carboxylic group was confirmed at around 13 ppm in CA-1 (Fig. 4).

![Figure 3. $^1$H-NMR spectra of CA-1 and CA-2 at around 4-7 ppm](image)

![Figure 4. $^1$H-NMR spectra of CA-1. A peak of carboxylic group was confirmed at around 13 ppm.](image)
3.2 Decomposition analysis of resist-A

Figure 5 shows HPLC charts of Resist-A before and after EB exposure. After exposure at the dose of 24 μC/cm², deprotected material (Deprot-1), which retention time coincided with the preparation, was observed at around 12 minutes. Furthermore, there was no significant product except for Deprot-1. From the HPLC analysis, it was found that main reaction at the exposed area of Resist-A film was deprotection of Prot-1 as shown in Fig. 6. The HPLC analysis result indicates that Resist-A including Prot-1 can generate polarity switching by deprotection per molecule. Followed by decomposition analysis, dissolution contrast of Resist-A was evaluated.

3.3 Lithographic evaluation

Figure 7 shows the contrast curve of resist-A. Resist-A exhibited good contrast. The E₀ value for resist-A was 24 μC/cm². The result suggests that Resist-A of just one protection per molecular resist material generates dissolution contrast sufficiently under general conditions by one deprotection reaction per molecule.

The lithographic performance of resist-A was evaluated using EB lithography. SEM images of patterns of lines and spaces for resist-A are shown in Fig. 8. Resist-A exhibited 30 nm hp resolution when the resist film thickness was 60 nm. Pattern collapse was observed at 25 nm hp. To estimate resolution limit, Resist-A of 40 nm film thickness also evaluated under same condition (Fig. 8 (b)). Resist-A exhibited 25 nm hp resolution without pattern collapse and partially resolved 20 nm hp at the exposure dose of 36μC/cm². As described in section 3.2, the pattern fabrication in Fig. 8 is accomplished by just one deprotection per molecule. This result suggests that deprotection reaction at the exposed and unexposed area is well controlled. From the results, potential resolution limit of the resists using the mechanism are expected to be improved as far as molecular size.

Figure 5. HPLC analysis of resist-A after and before exposure, (a); 0μC/cm² (b); 24μC/cm²

Figure 6. decomposition scheme of Prot-1 at the exposed area.

Figure 7. Contrast curve of Resist-A

EB exposure dose (μC/cm²)

Normalized film thickness

Figure 7. Contrast curve of Resist-A

The lithographic performance of resist-A was evaluated using EB lithography. SEM images of patterns of lines and spaces for resist-A are shown in Fig. 8. Resist-A exhibited 30 nm hp resolution when the resist film thickness was 60 nm. Pattern collapse was observed at 25 nm hp. To estimate resolution limit, Resist-A of 40 nm film thickness also evaluated under same condition (Fig. 8 (b)). Resist-A exhibited 25 nm hp resolution without pattern collapse and partially resolved 20 nm hp at the exposure dose of 36μC/cm². As described in section 3.2, the pattern fabrication in Fig. 8 is accomplished by just one deprotection per molecule. This result suggests that deprotection reaction at the exposed and unexposed area is well controlled. From the results, potential resolution limit of the resists using the mechanism are expected to be improved as far as molecular size.
dissolution contrast just one protecting group would be a key of 22 nm hp generation and beyond at the point of its high resolution.

References
1. ITRS Roadmap [http://www.itrs.net].

Figure 8. SEM images at each resist film thickness of Resist-A. FT is (a) 60 nm, (b) 40 nm.

3. Conclusion
Molecular resist material of Prot-1, which could work as CA resist was designed and synthesized. Resist-A showed good dissolution contrast by just one deprotection per molecule and resolved 25 nm hp without pattern collapse. The system generating