Development of New Negative-tone Molecular Resists Based on Calixarene for EUV Lithography

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We have developed new negative-tone molecular resists based on phenyl calix[4]resorcinarene derivatives, and evaluated their EUV patterning performance. EUV imaging experiments were performed using the high-numerical-aperture (NA = 0.3), small-field EUV exposure tool (HINA). Patterning results showed the resolution of the resist on an organic layer substrate to be 29 nm at an EUV exposure dose of 22.2 mJ/cm² and the obtainable aspect ratio to be as high as 2, with pattern collapse being markedly suppressed. In addition, we analyzed the outgassing of the resists during EUV exposure. The outgassing rates of the new resins were on the same order as that of conventional poly(p-hydroxy styrene) (PHS) resin. On the other hand, the outgassing rates of the new resists were about five times higher than that of conventional PHS-based resist. Quadrupole mass spectra showed the main source of resist outgassing to be EUV-induced decomposition of the photocid generator.

Keywords: EUV lithography, molecular resist, calix[4]resorcinarene, outgassing

1. Introduction

One of the most significant benefits of EUV lithography (EUVL) is that it is extendable to multiple technology rules (32 nm, 22 nm, and below). For the 32-nm rule and below, a difficult problem arises in that all the resist requirements (sub-30-nm resolution, high sensitivity, small line edge roughness (LER), no pattern collapse, and low outgassing) must be satisfied at the same time. At present, the development of high-quality EUV resists is one of top three critical issues in EUVL [1].

Considering resist materials, conventional polymeric chemically amplified (CA) resists have reached their performance limit [2]: The resolution is limited by acid diffusion, and the LER is too large due to the large molecules and compositional non-uniformity.

It is presumed that the cause of LER from the standpoint of the resist material is non-uniform dissolution, which gives rise to “aggregates” in the resist side wall [3, 4]. A promising solution is molecular resists, which have two strong points concerning reduction of the LER: One is the intrinsically small size of the molecules, which results in small “aggregates” and a small LER; and the other is monodispersion, which provides uniform dissolution and a small LER. In addition, regarding the properties of resist film, monodispersion is able to directly provide the designed function of a designed molecular structure. A large number of them have been investigated in the search for a suitable one [5-33].

Many papers have reported molecular resist systems based on various methyl calix[4] resorcinarene derivatives. However, the adhesion of such resists to a silicon wafer is rather poor; and in standard developer, the development rate is very high, necessitating either an extremely short development time or the use of dilute developer [8, 9, 15, 18, 20, 21].

Recently, the Cornell University group reported the good performance of positive-tone molecular resists based on partially protected p-tert-buty phenylcalix[4]resorcinarene derivatives in a process employing standard developer [22].

Generally speaking, positive-tone resists are more widely used than negative-tone ones in conventional optical lithography for LSI manufacturing. In EUVL, however, negative-tone resists may be better for delineating isolated patterns, such as those for the gate layer, because the serious issue of flare control makes a dark-field mask pattern preferable.

In this study, we developed new negative-tone molecular resists based on phenylcalix[4] resorcinarene derivatives, and evaluated both their EUV patterning performance and their outgassing characteristics during EUV exposure.
2. Experiments

2.1 Materials

Precursor: resorcinol (Kanto Chemical) and aromatic aldehyde derivatives (Mitsubishi Gas Chemical)

Photoacid generator (PAG): triphenylsulfonium perfluoro-1-butanesulfonate (TPS-PFBS, Midori Kagaku) and diphenylsulfonium p-toluene sulfonate (DPTMPS-PTS, Wako Pure Chemical Industries)

Cross-linker: hexamethoxymethylmelamine (MW-100LM, Sanwa Chemical)

Quencher: 2,4,5-Triphenyl-imidasole, (TPI, Kanto Chemical)

Casting solvent: propylene glycol monomethyl ether (PGME, Kanto Chemical)

Developer: aqueous solution of tetramethyl ammonium hydroxide (TMAHaq, Tokyo Ohka Kogyo)

Reference polymer: poly(p-hydroxystylene) (PHS, Mw = 8000, Aldrich)

2.2 Synthesis of phenylcalix[4]resorcinarene derivatives

The phenylcalix[4]resorcinarene derivatives were synthesized from resorcinol and a kind of aromatic aldehyde, as shown in Scheme 1.

R₁: methyl, phenyl, n-propyl, i-buty, i-propyl, cyclohexyl, or 4-n-propylcyclohexyl

R₂: H or methyl

Scheme 1

2.3 Formation of new negative-tone molecular resists

We first examined the solubility of phenylcalix[4]resorcinarene derivatives in PGME and 0.26N TMAHaq (Table 1): C-4-isopropylphenylcalix[4]resorcinarene (MGR104) and C-4-cyclohexylphenylcalix[4] resorcinarene (MGR108) showed good solubility in both PGME and 0.26N TMAHaq. Fig. 1 and 2 show the chemical structures and stable conformations of the new resins MGR104 and MGR108, respectively, yielded by molecular mechanics (MM2) calculations. The molecules of each resin are at most 2 nm long, which makes them suitable for a new negative-tone molecular resist system. Three advanced chemically-amplified (CA) resists (labeled A, B, and C) were prepared from four components: MGR104 or MGR108, a PAG, a quencher, and a cross-linker (Table 2).

Table 1. Solubility of phenylcalix[4]resorcinarene derivatives in PGME and 0.26N TMAHaq

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>PGME</th>
<th>0.26N TMAHaq</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>H</td>
<td>Insoluble</td>
<td>N/A</td>
</tr>
<tr>
<td>methyl</td>
<td>methyl</td>
<td>Insoluble</td>
<td>N/A</td>
</tr>
<tr>
<td>phenyl</td>
<td>H</td>
<td>Insoluble</td>
<td>N/A</td>
</tr>
<tr>
<td>n-propyl</td>
<td>H</td>
<td>Barely soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>i-butyl</td>
<td>H</td>
<td>Barely soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>i-propyl</td>
<td>H</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>cyclohexyl</td>
<td>H</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>4-n-propylcyclohexyl</td>
<td>H</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

a. Insoluble: < 2 wt%; Barely soluble: 2 - 5 wt%; Soluble: > 5 wt%
b. Insoluble: < 5 nm/min; Soluble: > 50 nm/min

Fig. 1. Chemical structure and stable conformation of C-4-isopropylphenylcalix[4]resorcinarene (MGR104).

Fig. 2. Chemical structure and stable conformation of C-4-cyclohexylphenylcalix[4]resorcinarene (MGR108).

Table 2. Components of new molecular resist systems.

<table>
<thead>
<tr>
<th>Resin</th>
<th>PAG</th>
<th>Quencher</th>
<th>Cross-linker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist A</td>
<td>MGR104</td>
<td>TPS-PFBS</td>
<td>TPI</td>
</tr>
<tr>
<td>Resist B</td>
<td>MGR104</td>
<td>DPTMPS-PTS</td>
<td>TPI</td>
</tr>
<tr>
<td>Resist C</td>
<td>MGR108</td>
<td>TPS-PFBS</td>
<td>TPI</td>
</tr>
</tbody>
</table>
2.4 Lithographic evaluation

To evaluate the sensitivity of EUV resists, we used an EUV flood-exposure tool [28]. The light source was a synchrotron radiation (SR) beam on the SBL-2 beamline of Super-ALIS at NTT [36]. A pair of grazing-incidence toroidal mirrors was installed near the front of SBL-2 to deliver and collimate the SR beam. The grazing angles of both were 2.5°. The tool was installed at the end station of SBL-2 and was equipped with a planar folding mirror, a Zr filter, an xy-wafer stage, and a load-lock mechanism in a vacuum chamber. The SR beam was incident on the folding mirror at an angle of 45°, and the reflected beam passed through the Zr filter to eliminate out-of-band light before arriving at the wafer. The mirror was coated with a 40-pair Mo/Si multilayer, which selects the band around 13.5 nm. The EUV exposure area was a circle 7 mm in diameter, and the EUV intensity on a resist was 0.4–1.8 mW/cm².

Imaging experiments were performed using the high-numerical-aperture (NA = 0.3), small-field EUV exposure tool (HINA) [34, 35]. HINA is equipped with an illumination system, projection optics, a mask stage, and a wafer stage in a vacuum chamber. The EUV light source was an SR beam on beamline SBL-1 of Super-ALIS. The exposure wavelength was 13.5 nm. The projection optics consist of two aspherical mirrors. The imaging field is 0.3 mm × 0.5 mm in size. The RMS wave front error (WFE) of the projection optics is 0.9 nm [37, 38].

HINA has both coherent and partially coherent illumination systems. The coherent one consists of two flat mirrors and a spherical mirror, which focuses the image of the EUV light source on a point at the pupil of the projection optics. The advantage of this system is that the image that it forms has a higher contrast than that obtainable with the partially coherent illumination system. So, we used it to investigate the ultimate fine-pitch patterning performance of the resist. The cut-off pattern half-pitch (hp) under three-ray interference is 28 nm for L&S patterns [35].

The EUV mask used in the experiments had an 80-nm-thick TaGeN absorber and a 10-nm-thick Cr buffer layer [39-41]. Sample resist films were spin-coated on either a silicon wafer or an organic-layer substrate and subjected to a post-application bake on a hot plate at a temperature of 110°C for 90 s. Following EUV exposure, the films were subjected to a post-exposure bake (PEB) at a temperature of 110°C for 90 s, developed in 0.26N TMAHaq for 30 s, and rinsed in deionized H₂O without a surfactant for 30 s using an off-line coater & developer system.

2.5 Measurements

FT-IR spectra of resist films were measured with a spectrometer (FTS-55A, Bio-Rad Digilab) by the attenuated-total-reflection method. The thickness of the films ranged from 50 nm to 100 nm, as determined with a multiwavelength interference thickness measurement system (M5100A, Nanometrics). Top-down images were taken with a critical-dimension (CD) SEM (S-8840, Hitachi).

Apparatus to evaluate EUV resist outgassing was installed on the SBL-2. It included a folding planar mirror, Zr filters, wafer stages, Bayard-Alpert gauges (Granville-Phillips), a quadrupole mass analyzer (M-200QA, ANELVA), and a load-lock mechanism in a vacuum chamber. The SR beam was incident on the folding planar mirror at an angle of 45° and passed through the Zr filter before reaching the resist.

The EUV exposure area was a 10 mm × 20 mm rectangle, and the EUV intensity on a resist was 0.01–2.0 mW/cm². The background pressure of the chamber was less than 1 × 10⁻⁷ Pa. The outgassing rates of resists in the steady state were determined by the pressure rise method, in which the outgassing rate is taken to be equal to the pumping-down speed during EUV exposure [31].

3. Results and Discussion

3.1 FT-IR spectra

Fig. 3 shows FT-IR spectra of resist C before and after exposure, and their difference. After EUV exposure at a dose of 50 mJ/cm² and PEB at 110°C for 90 s, the absorbance of the 980-cm⁻¹ band increased, which indicates the formation of an ether peak by a reaction between the cross-linker, hexamethoxymethylmelamine, and the o-alkylation of the phenolic structure [42]. Thus, EUV exposure makes the resist system work in a negative fashion.

3.2 Resist sensitivity

Fig. 4 shows EUV sensitivity curves for the three new molecular CA resists (A, B, C). All exhibit negative-tone characteristics: and the exposure doses providing a remaining thickness of 90% (E₉₀) were 71, 53, and 20 mJ/cm², respectively. Resists A and B showed poor sensitivity and no remaining thickness over 90%, even for an
overdose, such as 100 mJ/cm$^2$. On the other hand, resist C showed moderate sensitivity and a good, steep curve, indicating that it should exhibit good lithographic performance.

![FT-IR spectra of resist C film](image)

Fig. 3. FT-IR spectra of resist C film: a) before exposure (as-coated), b) after EUV exposure at dose of 50 mJ/cm$^2$ and PEB at 110°C for 90 s, and their difference (expanded 5×).

![EUV sensitivity curves](image)

Fig. 4. EUV sensitivity curves for three new negative-tone CA resists (A, B, C).

3.3 Fine-pitch patterning

Fig. 5 shows top views of dense lines with half pitches of 55, 50, 45, and 40 nm printed in a 55-nm-thick layer of resist B, which is based on MGR104, at an EUV exposure dose of 41 mJ/cm$^2$. Neither the resolution for 50 nm nor the sensitivity are satisfactory. One possible reason for the somewhat poor performance is the high development rate of the base resin, C-4-isopropylphenyl calix[4]resorcinarene in standard developer, 0.26N TMAHaq.

![Top view of dense line patterns with CDs ranging from 45 to 29 nm](image)

Fig. 5. Top view of dense line patterns with CDs ranging from 55 to 40 nm, printed in 55-nm-thick layer of resist B, which is based on C-4-isopropylphenyl calix[4]resorcinarene (MGR104), at EUV exposure dose of 41 mJ/cm$^2$. (hp = half pitch)

Fig. 6 shows top views of dense lines with half pitches of 45, 40, 35, 32, 30, and 29 nm printed in a 60-nm-thick layer of resist C, which is based on MGR108, at an EUV exposure dose of 26.4 mJ/cm$^2$. The resolution is less than 30 nm while the sensitivity is higher than that of resist A. Unfortunately, resist patterns with a half pitch of around 30 nm collapsed.

Fig. 7 shows top views of dense lines with half pitches of 45, 40, 35, 32, 30 and 29 nm printed in a 60-nm-thick layer of resist C on an organic-layer substrate at an EUV exposure dose of 22.7 mJ/cm$^2$. The patterns did not collapse, even for a half pitch of around 30 nm and a high aspect ratio (AR) of about 2.
Table 3 lists the outgassing rates of the three resists (A, B, C), their resins (MGR108, MGR104), a typical PHS-based KrF resist, and PHS in the steady state during EUV irradiation. The outgassing rates have been converted to equivalent values for the 400-mW/cm² EUV intensity of a mass-production exposure tool. The outgassing rate of the new molecular resist resins is in the same order as that of a conventional polymeric PHS resin. Unfortunately, the outgassing rates of the new molecular resists were about 5 times higher than that of a conventional polymeric KrF resist.

Fig. 9 shows quadropole mass spectra of the species outgassed from MGR108, PHS, and resist C films during EUV exposure. The spectra for PHS and MGR108 are almost the same and show no mass numbers over 44. These results indicate that MGR108 is as stable as PHS under EUV irradiation.

The mass spectrum of resist C shows much larger counts for mass numbers over 44 (48–53, 60–64, 69–70, 72–81) than either MGR108 or PHS. These fragments may be attributable to hydrocarbons (C₅H₁₀), hydrofluorocarbons (C₅H₇F₂), benzene derivatives, and sulfur oxide derivatives (SOₓ), which are the decomposition species of the PAG (TPS-PFBS). So, the main reason for the heavy outgassing of resist C is the decomposition of the PAG caused by EUV exposure.

Table 3. Outgassing rates of resist films in the steady state during EUV irradiation. The rates have been converted to equivalent values for the 400-mW/cm² EUV intensity of a mass-production exposure tool.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outgassing rate (molecules/cm²/s) at 400mW/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin (MGR104)</td>
<td>$4.7 \times 10^{14}$</td>
</tr>
<tr>
<td>Resist A</td>
<td>$3.2 \times 10^{16}$</td>
</tr>
<tr>
<td>Resist B</td>
<td>$1.8 \times 10^{16}$</td>
</tr>
<tr>
<td>Resin (MGR108)</td>
<td>$3.3 \times 10^{14}$</td>
</tr>
<tr>
<td>Resist C</td>
<td>$3.8 \times 10^{16}$</td>
</tr>
<tr>
<td>KrF resist *</td>
<td>$6.0 \times 10^{15}$</td>
</tr>
<tr>
<td>Resin (PHS)</td>
<td>$2.9 \times 10^{14}$</td>
</tr>
</tbody>
</table>

*Ref. 31)
Fig. 9. Quadrupole mass spectra of species outgassed from MGR108, PHS, and resist C films during EUV exposure.

4. Conclusions

We developed new negative-tone molecular resists based on phenyl calix[4]resorcinarene derivatives and evaluated their EUV patterning performance. The patterning results for resist C, which is based on C-4-cyclohexylphenylcalix[4] resorcinarene (MGR108), on an organic layer substrate showed the resolution to be 29 nm at an EUV exposure dose of 22.2 mJ/cm², and the obtainable aspect ratio to be as high as 2.

The outgassing rates of the new resins were on the same order as that of a conventional resin, PHS. On the other hand, the outgassing rates of the new molecular resists were about 5 times higher than that of a conventional PHS-based resist. The main cause of resist outgassing is the EUV-induced decomposition of the PAG.

If a low-outgassing PAG can be applied, this molecular resist system has the potential to meet the strict resist requirements for the 32-nm technology node and beyond.

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References