Optimization of a Top-Surface Imaging Process for 193-nm Lithography

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We investigated the effect of silylation agents, silylation process, and silylation thickness on lithographic performances and optimized the TSI process for the device development. TMS type silylation agents are much preferable than DMS type ones because of the excellent stability after silylation. Thicker silylation process not only improves the line edge roughness (LER) and the mask linearity but also reduce the critical dimension (CD) variation induced by the fluctuation of silylation thickness. However, additional improvements for the silylation thickness control are necessary to achieve a CD uniformity of ±10nm across a wafer.

Keywords: ArF lithography, Silylation, Top Surface Imaging, Line Edge Roughness, Linearity, Dry development

1. Introduction

As a resist process for the next-generation lithography, the Top-Surface Imaging (TSI) technique has been proposed. In particular, TSI using ArF excimer laser lithography at a wavelength of 193 nm is a leading candidate as the mass production tools for 0.10-µm-rule devices. Furthermore, the application of TSI to proximity X-ray or broadband EUV (13–40 nm) lithography is expected for printing 0.07-µm-rule devices. To date, many articles have demonstrated the excellent resolution and process margin of TSI, but there are still many problems to be studied and solved before it can be applied to actual device fabrication processes. Among them the stability and uniformity are important factors, although these have not been discussed well. This paper focuses on the stability and uniformity of silylation process and describes the results of optimizing TSI for the application to device fabrication processes.

2. Experimental

MX-P7 from Microlithography Chemical Corp. was used as the TSI resist for 193-nm lithography. MX-P7 was spin coated onto HMDS-treated silicon wafers and exposed by a prototype ArF excimer laser stepper (NA=0.55). A vapor-phase silylation process was carried out using a Microstar 200C (GENESIS). In this study, we evaluated the following commercially available silylation agents: dimethylsilyl dimethylamine (DMSDMA), trimethylsilyl dimethylamine (TMSDMA), trimethylsilyl diethylamine (TMSDEA), and 1,1,3,3-tetramethyl disilazane (TMDS). All these silylation agents were obtained from Shin-Etsu Chemical Corp. Their chemical structures are shown in Fig. 1.

![Figure 1. Chemical structures of silylation agents.](image-url)
In order to monitor the silylation content in the resist, we measured the absorbance at 920 cm⁻¹ (Si-O-aryl) by Fourier transform infrared (FT-IR) spectroscopy. An ECR etcher M328SX (Hitachi) and TCP etcher Alliance 9400PTX (Lam Research) were used for the dry development processes. The M328SX was used to measure the resist contrast and the 9400PTX was used for the actual image patterning. The silylation thickness was measured with an optical thin film monitor TF-1 (KLA-Tencor). The critical dimensions (CDs) and LER were measured with a KLA8100 scanning electron microscope (SEM), and the cross-sectional pattern profiles were observed with a Hitachi S-4100 SEM. The experimental conditions are listed in Table 1.

### Table 1 Process parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>HMDS treated silicon wafers</td>
</tr>
<tr>
<td>Prebake</td>
<td>120°C, 90sec</td>
</tr>
<tr>
<td>Resist</td>
<td>0.75 μm MX-P7</td>
</tr>
<tr>
<td>Exposure</td>
<td>Nikon ArF stepper 0.55NA</td>
</tr>
<tr>
<td>Mask</td>
<td>Conventional binary mask</td>
</tr>
<tr>
<td>Silylation</td>
<td>60–120°C, 30–180sec, 15–80Torr</td>
</tr>
<tr>
<td>Dry Dev. (9400PTX)</td>
<td>BT: 5mT7/200TCP/2BP/36CF4/15O2/20s</td>
</tr>
<tr>
<td></td>
<td>ME: 5mT7/500TCP/2BP/15O2/80O2/70s</td>
</tr>
<tr>
<td></td>
<td>CE: 5mT7/300TCP/36CF4/30O2/60O2/25s</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

#### 3.1. Silylation agents

In order to evaluate the effect of silylation agents on the lithographic resolution, we measured the silylation contrasts and the development contrasts. Figure 2 shows the IR absorbance of exposed and silylated MX-P7. The silylation content of TMDS was too low to measure the silylation contrasts. From these IR absorbances, the silylation contrasts were calculated by the following equation.

\[
\gamma_{\text{silylation}} = \frac{a_{\text{max}} - a_{\text{min}}}{a_{\text{max}} + a_{\text{min}}} \tag{1}
\]

In this equation, \(a_{\text{max}}\) means the IR absorbance of unexposed resist and \(a_{\text{min}}\) means the IR absorbance of sufficiently exposed resist. Ideally \(a_{\text{min}}\) must be 0, because no silylation should occur in a sufficiently exposed resist film. However, Figure 2 shows that all the evaluated silylation agents silylated even the highly exposed resist film. This result indicates that these commercially available silylation agents need the pretreatment to remove the silicon residue formations.

Because of these considerations, we always performed the first 10–20 s breakthrough (BT) etching using fluorine gas to remove the skin surface of silylated resist before the main etching (ME) using oxygen gas to remove the unsilylated resist. As an example, the normalized thickness after the dry development is shown in Fig. 3. DMSDMA was used as the silylation agent in this example.

The dry development contrasts were calculated by the following equation.

\[
\gamma_{\text{development}} = \frac{\partial NT}{\partial \log E} \bigg|_{NT=1} \tag{2}
\]

where NT means the normalized thickness. The calculated silylation contrasts are listed in Table 2. All silylation agents take the same silylation contrast (\(\gamma_{\text{silylation}}\)) values. The development contrasts (\(\gamma_{\text{development}}\)) of these silylation agents
range from 19 to 36. The required optical contrast of photoresist is theoretically calculated from the development contrast by the following equation\(^6\).

\[
\text{Optical Contrast} = \frac{10^{17} - 1}{10^{17} + 1} \quad (3)
\]

According to this equation, the resolution limit of photoresist saturates more than 12 of \(\gamma_{\text{development}}\). These results indicate that the lithographic resolutions of these silylation agents are comparable.

Figure 4 shows the time dependency of IR absorbances of the unexposed resist after silylation.

![Figure 4. IR absorbances of silylation agents as a function of number of days since silylation.](image)

Though the IR absorbances of the silylation agents having tri-methyl groups did not change, that having di-methyl groups decreased linearly with time. These results suggest that DMS is not stable as the protecting group of phenol and that de-silylation occurred. On the other hand, TMS is stable as the protecting group of phenol\(^7\) and no de-silylation occurred\(^8\). At the R&D stage, researchers do not have to be conscious of this de-silylation of silylated resist because silylated wafers are rarely left for a long time before dry development process for various reasons such as machine troubles. Therefore, TMS-type silylation agents are much better for the actual device fabrication process than DMS-type ones.

### 3.2 Silylation thickness

This section describes the effect of silylation thickness on lithographic performances. Figure 5 shows the relationship between the silylation thickness and the optimum exposure dose \((E_{\text{opt}})\) of 180-nm and 160-nm lines/spaces.

![Figure 5. \(E_{\text{opt}}\) of 180-nm and 160-nm lines/spaces. It varied from 90 to 180 mJ/cm\(^2\) with changing silylation thickness.](image)

Since a thinner silylation layer results in a smaller line width after dry development, the resist sensitivity becomes higher. In this study the silylation thickness was changed from 120 to 290 nm, \(E_{\text{opt}}\) was changed from 90 to 190 mJ/cm\(^2\). Another explanation is that the CD of the pattern feature is very sensitive to the silylation thickness variations.

Figure 6 shows the relationship between the depth of focus and the exposure latitude of a 160-nm L/S pattern. Both the depth of focus and exposure latitude were calculated by the definition of the CD tolerance as \(\pm 10\%\) of the designed pattern size.

### Table 2 Measured contrasts of each silylation agents.

<table>
<thead>
<tr>
<th>Silylation pressure</th>
<th>DMSDMA</th>
<th>TMSDMA</th>
<th>TMSDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature &amp; time</td>
<td>100°C × 60s</td>
<td>120°C × 90s</td>
<td>120°C × 90s</td>
</tr>
<tr>
<td>Silylation contrast</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Development contrast</td>
<td>25</td>
<td>19</td>
<td>36</td>
</tr>
</tbody>
</table>
These curves are similar and the optimized thickness exists around 170 nm. Too thinner silylation layer short in the etching durability as the mask for the under layer and induces the smaller process margin.

Figure 7 shows the relationship between the mask linearity and the silylation thickness. The Eopt of 180-nm lines/spaces were employed for each exposure.

A thicker silylation layer improves the mask linearity. This can be seen more clearly in the relationship between the silylation thickness and the CD of 140-nm L/S shown in Figure 8. As the silylation thickness increases, the CD becomes close to the designed pattern size.

The reason why thicker silylation condition results in better mask linearity is understood as follows. Figure 9 shows the simulated aerial image of 130, 200, and 500-nm lines/spaces. The CD after dry development is predicted by cutting this aerial image by a slice level. In this case, the slice level corresponds to the threshold value to crosslink the resist film. When the intensity is higher than this slice level, exposed resist is crosslinked and therefore not silylated. Consequently the resist is removed by dry development. The changing exposure dose means the value of this slice level. The lower exposure dose corresponds to the higher slice level. The calculated CDs by various slice levels are listed in Table 3.

<table>
<thead>
<tr>
<th>Slice level</th>
<th>130-nm L/S</th>
<th>200-nm L/S</th>
<th>500-nm L/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 µm</td>
<td>0.10 µm</td>
<td>0.17 µm</td>
<td>0.50 µm</td>
</tr>
<tr>
<td>0.30 µm</td>
<td>0.15 µm</td>
<td>0.19 µm</td>
<td>0.52 µm</td>
</tr>
<tr>
<td>0.35 µm</td>
<td>0.22 µm</td>
<td>0.21 µm</td>
<td>0.52 µm</td>
</tr>
</tbody>
</table>

Table 3. Calculated CDs of lines/spaces by various slice levels.
Figure 11 shows the relationship between the Line Edge Roughness (LER) and the silylation thickness. After measuring the line width for 32 points within a SEM image, we statistically calculated the LER from the following equation.

\[ \text{LER} = W_{\text{max}} - W_{\text{min}} \]  

(Rounded silylation edges are important for the good LER control. When the silylation layer is too thin, the edges look like “bird’s peak” and this results in large LER.)

Table 4 shows the common ED-window of 180-nm lines/spaces and isolated lines. The common exposure latitude decreases with the silylation thickness.

Figure 13 shows the relationship between the actual CD of 160-nm L/S and the silylation thickness.

LER drastically degrade less than 140-nm silylation thickness. Figure 12 explains this reason.
The tendencies of each curve in Figure 13 mean the effects of the fluctuation of silylation thickness on the CD variation. The CD variation is reduced by thicker silylation process. The CD variation per 1-nm change of silylation thickness (ΔCD/ΔST), and the silylation latitude required to achieve CD variations of ±5 nm were calculated from these data. They are shown in Figure 14.

The ΔCD/ΔST decreases and the silylation latitude is increased by a thicker silylation condition. However, required latitude is less than 3%. For vapor-phase silylation, the silylation thickness is determined by three parameters: the temperature, pressure, and time of silylation. Figures 15 shows the silylation uniformity across a 200-mm wafer as a function of the silylation pressure and silylation time.

![Figure 14](image_url)

**Figure 14.** CD variation induced by the fluctuation of silylation thickness and required silylation uniformity for ±5 nm CD variation.

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![Figure 15](image_url)

**Figure 15.** Silylation time and uniformity. DMDSMA was used as a silylation agent and all silylation temperatures were 100°C.

By measuring the thickness differences at 49 points before and after silylation \( \Delta T = T_{\text{silylation}} - T_{\text{initial}} \) across a wafer using an optical thin film monitor, we calculated the silylation uniformity by the following equation from the average value \( \Delta T_{\text{average}} \), the maximum value \( \Delta T_{\text{max}} \), and the minimum value \( \Delta T_{\text{min}} \).

\[
\text{Uniformity} = \frac{\Delta T_{\text{max}} - \Delta T_{\text{min}}}{2 \times \Delta T_{\text{average}}} \quad (5)
\]

The silylation uniformity across a wafer improves drastically until 90 s, and then remains constant with silylation time at a value of 3.5%. Because of these considerations, we fixed the silylation time 120 s and investigated the relationship between the CD uniformity across a wafer and the silylation thickness by changing the silylation pressure and temperature.
Figure 16 shows the relationship between the CD uniformity of a 160-nm lines/spaces and the silylation thickness. This CD variation includes not only the silylation fluctuation but also all other process fluctuations such as the dry development, resist coating, and ArF exposure.

By measuring the CDs 25 points across a 200-mm wafer using a top-down SEM, we calculated the CD uniformity by the following equation from the average value \( \text{CD}_{\text{average}} \), the maximum value \( \text{CD}_{\text{max}} \), and the minimum value \( \text{CD}_{\text{min}} \).

\[
\text{Uniformity} = \frac{\text{CD}_{\text{max}} - \text{CD}_{\text{min}}}{2 \times \text{CD}_{\text{average}}} \quad (6)
\]

It is obvious from Figure 16 that the thicker silylation drastically improves the CD uniformity across a wafer. Finally CD uniformity of ±4.1% across a wafer was achieved. However, the best silylation uniformity is ±3.5% by the current silylation equipment, therefore silylation fluctuation occupies the most part of the CD variation. TSI's high resolution and large process margin have been demonstrated by many articles. In order to apply this technique to the device fabrication processes, the CD variation induced by the fluctuation of the silylation thickness must be well controlled. However, the current equipment does not have the enough performances to accomplish the CD uniformity required for the next-generation lithography.

The step to demonstrate the advantages of TSI technique has been finished. In the next step, both process engineers and machine engineers must think the method to control this technique with same level of conventional mono layer resist processes.

All the relationships between the silylation thickness and the lithographic performances obtained in this study are summarized in Table 5.

<table>
<thead>
<tr>
<th>Silylation thickness</th>
<th>Thin</th>
<th>Thick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>Good</td>
<td>Bad</td>
</tr>
<tr>
<td>ED window of L/S</td>
<td>Optimum thickness exists</td>
<td></td>
</tr>
<tr>
<td>Mask linearity</td>
<td>Bad</td>
<td>Good</td>
</tr>
<tr>
<td>Line Edge Roughness</td>
<td>Bad</td>
<td>Good</td>
</tr>
<tr>
<td>Iso/dense ED-window</td>
<td>Good</td>
<td>Bad</td>
</tr>
<tr>
<td>Silylation margin</td>
<td>Bad</td>
<td>Good</td>
</tr>
</tbody>
</table>

Figure 16. Silylation thickness and CD uniformity of a 160-nm L/S across a 200-mm wafer.

Table 5. Relationship between the silylation thickness and lithographic performances.

4. Conclusions
We studied the effects on lithographic performances of silylation agents, silylation process, and the silylation thickness. De-silylation occurred as time passed after silylation when DMS type silylation agents were used, but not when TMS type silylation agents were used. The mask linearity, LER, and silylation margin were improved by the thicker silylation process. By optimization of a silylation thickness, the CD uniformity of a 160-nm L/S across a 200-mm wafer of ±4.1% was achieved. Additional improvement of the silylation uniformity is necessary to achieve the CD variation of ±10nm.

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References


