Recent Progress of EUV Resist Technology in EIDEC

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EUV lithography is one of the promising technologies for manufacturing devices at 16 nm half-pitch node and below. EUV resists are required to improve the resolution, line width roughness (LWR), and sensitivity. However, it is generally thought that the lithographic performance is determined by the trade-off relationship among these factors. Moreover, resist outgassing is another issue with EUV resists, as the outgassing of resists during EUV exposure can cause carbon contamination on EUV mirrors, thereby degrading its reflectivity. This paper outlines the recent progresses in EUV resist technology at the EUVL Infrastructure Development Center.

Keywords: EUV, Lithography, Resist, Resist process, Outgas, Contamination

1. Introduction

EUV lithography is one of the promising technologies for manufacturing devices at 16 nm half-pitch node and below. Some resists recently have shown the potential of 16 nm half-pitch resolution [1, 2]. Nevertheless, the trade-off relationship among resolution, line width roughness (LWR), and sensitivity still continues to be a problem in the development of resists for EUV [3]. EUV light sources are often required to increase its power to facilitate high volume manufacturing. However, the technological difficulties still remain [4]. Therefore, EUV resists with high sensitivity are highly imperative to compensate the low power of EUV light and obtain sufficient throughput.

Moreover, resist outgassing is another major problem. In general, resist outgas consists of hydrocarbons that are generated in resists during EUV exposure. These hydrocarbons deposit on EUV mirrors and form carbon contamination films, which tend to degrade the reflectivity of EUV mirrors. The EUV scanner supplier has proposed a method for evaluating resist outgassing using witness samples (WS) [5]. Figure 1 shows the schematic of the protocol proposed for evaluating the resist outgas. The contamination film is formed on WS by EUV light or electron beam. Following that, the amount of outgassing for cleanable components is quantified by measuring the contamination film thickness. After subsequent
hydrogen cleaning of contamination films on WS, non-cleanable elements are analyzed and quantified by X-ray photoelectron spectroscopy (XPS). There are two irradiation sources; the EUV light and electron beam (EB), for the resist exposure. The EB source system is preferable due to its high throughput.

The EUVL Infrastructure Development Center (EIDEC) is developing EUV resist materials and processes and researching resist outgassing for 16 nm node and beyond. This paper outlines the recent progresses in EUV resist technology at EIDEC.

2. Experimental Conditions

2.1. Lithographic Evaluations

Small-field exposure tool (SFET) with the numerical aperture of 0.3 and the annular illumination of 0.7/0.3 (σ outer / σ inner) was used for EUV exposure [6]. Resist coating and baking are performed using Clean Track Act 12 instrument (Tokyo Electron Ltd.). CD measurement was performed using a Hitachi CG4000 scanning electron microscope (SEM).

Resists were applied to 300 mm wafers treated with HMDS or coated under-layers. For positive tone resists, 0.26 N tetramethylammonium hydroxide (TMAH) aqueous solution was used as the coater/developer, while the puddle of n-butyl alcohol in Litho Spin Cup 300D (Litho Tech Japan Co.) was used as the developer for negative tone resists.

2.2. Resist Outgas Evaluation Conditions

EIDEC has both EB- and EUV-based resist outgas evaluation tools. The EB-based evaluation tool, EUVOM-9000 (Litho Tech Japan Co.), is located at Tsukuba Japan. The EUV-based tool is set up at the beamline 9 of NewSUBARU which is the synchrotron radiation facility of the University of Hyogo [7-13]. The resist thicknesses were 60 nm. 1 inch Ru-capped silicon wafers were used as WS. Hydrogen cleaning after CG evaluation was performed using a built-in cleaning unit in EUVOM-9000. Contamination film thicknesses on WS were measured using spectroscopic ellipsometer (SE; M-2000X, J.A. Woollam Co.). The non-cleanable elements on WS remaining after hydrogen cleaning were determined using XPS (PHI 5000 VersaProbe II: ULVAC-PHI Inc.).

3. Results and Discussion

3.1. Lithographic Evaluation

In FY 2013, EIDEC selected new standard resists, namely, ESR4 (positive-tone resist) and ESR5 (negative-tone resist). Figure 2 shows the lithographic performance of ESR1, ESR4, and ESR5 upon exposure to SFET. As is seen, ESR4

<table>
<thead>
<tr>
<th>Resist</th>
<th>ESR1</th>
<th>ESR4</th>
<th>ESR5</th>
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</thead>
<tbody>
<tr>
<td>Type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution (nm)</td>
<td>25</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>LWR (nm)</td>
<td>8.1</td>
<td>7.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Sensitivity (mJ/cm²)</td>
<td>12.2</td>
<td>15.8</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Top-Down SEM Image
30nm L/8 (Mag. 200k)

Figure 2. Newly selected EIDEC standard resists; ESR4 and ESR5
and ESR5 show lower sensitivity than that of ESR1. Nevertheless, ESR4 and ESR5 show improved LWR. In particular, ESR5 shows over 25% improvement in LWR. The negative-tone resists have been reported to show less swelling characteristics than the positive-tone resists during development [14–17]. This characteristic is considered to affect the improvement of LWR after development.

3.2. Resist Outgas Evaluation
EIDEC uses model resists for evaluating the resist outgas. Table 1 lists the model resists prepared for evaluating the contribution of resist components on the cleanable contaminants [18]. Two types of polymers with an acid labile protecting unit (PU) and an acid stable protecting unit were employed. The PAG concentration is 20 wt.% of the polymer and the quencher concentration is 0.1 mol of PAG. Upon evaluating contamination film thicknesses, we evaluated the contribution of PAG and PU decompositions, which were formed by acid decomposition during exposure. The evaluation was performed using the EB- and EUV-based outgas evaluation tools. The corresponding results are shown in Figure 3. Results confirm that the main contributor in the contamination film is PAG decomposition.

<table>
<thead>
<tr>
<th>Model Resist</th>
<th>Polymer</th>
<th>PAG</th>
<th>Quencher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>Acid labile unit</td>
<td>None</td>
<td>Tri-n-octylaniline</td>
</tr>
<tr>
<td>PAG free</td>
<td>Acid labile unit</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>PU free</td>
<td>Acid stable unit</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>PAG and PU free</td>
<td>Acid labile unit</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

Moreover, the EB-based test results well agreed with those of the EUV-based test. This method clearly indicates the resist component that needs to be controlled to reduce resist outgassing. Table 2 lists the model resists used for evaluating the non-cleanable contaminants. In the typical process, four types of PAG were prepared to compare the cleanability of the non-carbon elements, namely, sulfur, indium, chlorine, and bromine in contamination films [19]. Model resist S contains PAG with 30 wt.% of polymer, while the PAG concentrations in other model resists are equimolar. The cleanability is defined as the ratio

<table>
<thead>
<tr>
<th>Model Resist</th>
<th>Polymer</th>
<th>Quencher</th>
<th>PAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td></td>
<td>[Structure]</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>[Structure]</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td>[Structure]</td>
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<tr>
<td>Br</td>
<td></td>
<td>[Structure]</td>
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</tbody>
</table>

Figure 4. Cleanability of the non-cleanable elements after hydrogen cleaning

![Figure 3. Estimated results of the contribution of resist components in the contamination film](image-url)
cleaning to the initial amount. We also measured the cleaning rate of the contamination film. The evaluation was performed using both EB- and EUV-based outgas evaluation tools. Figure 4 shows the cleanability of model resists, normalized to that of sulfur. As is seen, chlorine and bromine in the contamination film could be cleaned by hydrogen cleaning, in the case of both EB- and EUV-based tests. On the other hand, sulfur and iodine continue to remain as non-cleanable elements on WS. In particular, iodine generated in the EB-based test could not be cleaned by the hydrogen cleaning process. It is thought that the cleanability of the non-carbon contaminants is related to the reaction of the hydrogen radicals during cleaning, and the volatility of the hydrides. Among these non-cleanable elements, iodine has the smallest electronegativity and the lowest boiling point of its hydride gas. The electronegativities and boiling points of chlorine and bromine are greater than those of sulfur and iodine. Therefore, chlorine and bromine are readily reduced during the hydrogen cleaning process, which subsequently desorb from WS surface.

Figure 5 shows the contamination films’ cleaning rate. As is seen, the cleaning rates of contamination films in the EUV-based test are faster than those in the EB-based test in all the cases. Furthermore, as shown in Figure 4, the cleanabilities of sulfur and iodine in the EUV-based test are larger than that in the EB-based test. These results suggest that the contamination film in EUV-based tests is more porous than that in the EB-based test. From this perspective, further analyses are needed in the future.

4. Conclusion

This paper outlines the recent progresses in EUV resist technology at EIDEC. EIDEC has selected new EIDEC standard resists with good LWR. Using model resists, the contribution of resist components to the cleanable contamination was analyzed in the evaluation of resist outgas. This method vividly clarifies the main contributor in the resist component that needs to be eliminated to reduce resist outgassing. Also, the cleanabilities of the non-carbon elements were evaluated. Results indicate that iodine is the critical non-cleanable element that contributes to the reflectivity loss in EUV mirror. On the basis of the results obtained, the guidelines for designing the resist material are indicated.

5. Acknowledgement

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References


