Evaluation of the Outgassing from Resists at the EUV Wavelength

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One of the important issues in EUVL is the outgassing problem because the contamination caused by the resist outgassing decreases the reflectivity of the reflective mask and the imaging optics. In this report, we evaluated the resist and resin outgassing at EUV wavelength by the quadrupole mass spectrometer (QMS) and the adhesion to surface of Mo/Si substrate or Si substrate from outgassing by the time-of-flight secondary ion mass spectrometry (TOF-SIMS). The samples were four typical kinds of polymers.

As a result of QMS-measurement, it was found that the mainly outgassing species detected are carbon oxide (28 amu) and hydrocarbon.

As a result of TOF-SIMS measurement, Si (28) due to the substrate were mainly detected in spite of resist or resin sample. TOF-SIMS data have not interrelation to QMS data for these experiments. So, it was found that outgassing materials detected by QMS are little on the surface of the Mo/Si or Si substrate.

Keywords : EUVL, contamination, resist, outgassing, adhesion, QMS, TOF-SIMS

1. Introduction

Extreme ultra-violet lithography (EUVL) [1] is one of the candidates to fabricate a sub-0.05 \( \mu \)m-pattern. The absorption coefficients of the resist material are large at the wavelength of 13.5 nm. Thus, as shown in Figure 1, it is proposed mainly three kinds of resist material processing technologies for (1) the ultra thin single layer resist, (2) the silicon containing bi-layer resist, and (3) the silylation resist for top surface imaging [2-3]. We have been developing these three technologies for EUVL. In these processes, especially, the single layer resist processing technology is very important to save the lithographic costs. So, we have investigated the absorption to the resist by the simulation, the patterning characteristics and line edge roughness of the single-layer-resist. As a result, it is found that Chemically amplified resist for KrF is applicable to fabricate a sub-0.05 \( \mu \)m-pattern.

However, one of the important issues in EUVL is the outgassing problem because the contamination caused by the resist outgassing decreases the reflectivity of the reflective mask and the imaging optics [4-5].

The factors of generating contamination are four as shown in Figure 2.

One factor is due to the outgassing from the resist that is diffused in vacumm environment.

Two is to adhere to surface of the reflective mirror by the outgassing from the resist.

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Three is to change the quality of the materials adhered from outgassing by EUV exposure.
Four is to adhere some materials to the surface of the reflective mirror by CVD (chemical vapor deposition) of EUV exposure.

The outgassing chamber is consist of three chambers, the mirror chamber with Mo/Si-reflective-mirror, the sample chamber with resist sample and the QMS chamber with quadrupole mass spectrometer (M-QA200F; ANELVA Co., Ltd), shown in Figure 4.

2. Experiment
2.1 Equipment
We constructed the chamber for outgassing experiments which was located at EUVL beamline of ASET. This beamline are shown in Figure 3.

The EUVL beamline is consist of filter chamber, plane mirror, outgassing chamber and High-NA exposure system. The 0.2 μm-thick beryllium is installed in the filter chamber that is located at upstream from the outgassing chamber.

2.2 Evaluation Method
2.2.1 Outgassing Measurement by QMS
As shown in Figure 4, the SR light is reflected on Mo/Si mirror in the mirror chamber and the reflected light exposes the resist sample in the sample chamber. In the same time, it was measured the mass spectra of outgassing in the range of 0-100 amu by the quadrupole mass spectrometer in the QMS chamber.

The exposure area on a resist sample is 10mm × 5mm in size. It is kept that the base pressure in QMS chamber is 1.0 × 10^{-6} Pa during the experiment, and the base pressure in sample chamber is 7.0 × 10^{-6} Pa.

2.2.2 Outgassing-adhesion Measurement by TOF-SIMS
As shown in Figure 4, the SR light is reflected on Mo/Si mirror in the mirror chamber and the reflected light exposes the resist sample in the sample chamber. In the same time, outgassing from the resist sample adheres to Mo/Si-multilayer-substrate or Si-substrate that was set at 10mm from the resist sample forward to the QMS chamber. Then, the materials adhered on surface of Mo/Si-substrate or Si-substrate from outgassing is estimated by the TOF-SIMS.

2.3 Sample
The samples were four typical polymers or resists as shown Table 1. Thickness of the polymers or resists film is all 200nm.

Table 1 Resist or polymer sample and the condition of pre bake.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre Bake</th>
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<tbody>
<tr>
<td>(a) ZEP520</td>
<td>190°C 180sec</td>
</tr>
<tr>
<td>(b) ESCAP type resist</td>
<td>130°C 90sec</td>
</tr>
<tr>
<td>(c) Novolak type resin</td>
<td>100°C 90sec</td>
</tr>
<tr>
<td>(d) Si-Contained resist</td>
<td>110°C 90sec</td>
</tr>
</tbody>
</table>

(a) ZEP520 (Nippon Zeon Co.,) is non-chemical amplified resist. The base resin of ZEP520 consists of a copolymer of chloromethacrylate and methylstyrene.
(b) ESCAP type resist is chemical amplified resist and the base resin contains of a copolymer of PHS and t-BMA.
(c) Novolak type resin is base resin for i-line or EB.
(d) Si-contained resist is the upper layer used to typical Bi-layer resist. The Si content is about 8%.

3. Result and Discussion
3.1 Mass Spectrometry (MS) Data
Figure 5 shows the MS data of ZEP520. It shows Mass Number versus Ion Current. The MS data is the difference between the MS data before exposure and that just after exposure. The mainly outgassing species detected are carbon oxide (28 amu), chlorine (35 amu) and methane (15 amu). By the EUV exposure, the sub-chain of chloromethacrylate is decomposed as shown in Figure 5.

Figure 6 shows the MS data of ESCAP type resist. The mainly outgassing species detected are carbon oxide (28 amu), carbon (12 amu) and methane (15 amu). By the EUV exposure, the sub-chain of t-BMA is decomposed as shown in Figure.

Figure 7 shows the MS data of Novolak type polymer. The mainly outgassing species detected are carbon oxide (28 amu) and methane (15 amu). By the EUV exposure, the sub-chain of benzene is decomposed as shown in Figure. The peak of carbon oxide is small because there are no CO-gas in decomposed polymer.

Figure 8 shows the MS data of Si-contained resist. The mainly outgassing species detected are carbon oxide (28 amu) and CH₃ (16 amu).
To compare outgassing quantity of all samples, that of ZEP520 and Si-contained resist are large and ESCAP type resist and Novlak resin are small.

3.2 TOF-SIMS Data
We investigated the outgassing adhesion to surface of Mo/Si-substrate or Si-substrate by the TOF-SIMS.

Figure 9 shows the TOF-SIMS data of ZEP520 on Mo/Si-substrate surface. It shows Mass Number versus total counts of positive secondary Ion. It found that these detected peaks are able to distinguish two kinds.

(a) ZEP520

(b) ESCAP type resist

(c) Novolak type resin

(d) Si-contained resist

Figure 11 TOF-SIMS data of four samples
One kind of peaks is the decomposition of polydimethylsiloxane (PDMS) as SiH (29 amu), SiCH₃ (43 amu) and Si(CH₃)₃ (73 amu). PDMS is a main component of Si-contained oil that is used to rotary pomp. So, this PDMS was seemed to adhere in making a vacuum of the vacuum chamber.

Another kind is hydrocarbon (CₓHᵧ) as CH₃ (15), C₂H₅ (27), C₃H₅ (41), C₄H₉ (44), C₅H₁₁ (57) and C₈H₁₇ (81).

So, it was seemed that CₓHᵧ is adhered by the outgassing from sample or the contamination from the vacuum chamber.

Figure 10 shows the TOF-SIMS data of ZEP520 on Mo/Si and Si-substrate surface. It was found that both Mo/Si and Si substrate are detected to same species. So, the adhesion from each sample is able to be evaluated with Si substrate.

Figure 11 shows the TOF-SIMS data of four sample. (a) is ZEP520, (b) is ESCAP type resist, (c) is Novolak type resin and (d) is Si-contained resist. These data were the deference between the TOF-SIMS data of substrate-surface with adhesion and without adhesion and were normalized by the peak of Si (28).

To compare with four data, Si (28) due to the substrate were mainly detected in spite of resist or resin sample. TOF-SIMS data have not interrelation to QMS data for these experiments. So, it was found that outgassing materials detected by QMS are little on the surface of the Si substrate.

4. Conclusion

The resist and resin outgassing at EUV wavelength were measured by the quadrupole mass spectrometer and the adhesion to surface of Mo/Si substrate or Si substrate from outgassing were measured by the TOF-SIMS.

The samples were four typical kinds of polymers or resists as ZEP520, ESCAP type resist, Novolak type resin and Si-contained resist.

As a result of QMS-measurement, it was found that the mainly outgassing species detected are carbon oxide (28 amu) and hydrocarbon.

As a result of TOF-SIMS measurement, Si (28) due to the substrate were mainly detected in spite of resist or resin sample. TOF-SIMS data have not interrelation to QMS data for these experiments. So, it was found that outgassing materials detected by QMS are little on the surface of the Si substrate.

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Reference


