The Photo-absorption Coefficient Measurement of EUV Resist

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We evaluated the transmittance and the sensitivity of the chemically amplified (CA) resist including various kind of photo acid generator (PAG) to clarify cause-and-effect relationship between the photo-absorption of PAG and the sensitivity under extreme ultraviolet (EUV) exposure. Transmission measurements and sensitivity measurements were carried out at the BL10 and BL3 beamlines in NewSUBARU synchrotron radiation facility. It is confirmed that increasing the atomic absorption cross section of an anion of PAG is effective in improving the sensitivity of the CA resist in EUVL.

Keywords: resist, EUV, transmission, absorption coefficient, sensitivity

1. Introduction
The extreme ultraviolet lithography (EUVL)[1] is the most effective technology to realize the semiconductor mass production technology since half-pitch (hp) 22nm node and below. The top three critical issues of EUVL are 1) the high power and the stability of EUV light source, 2) the mass production of the defect-free mask, 3) the resist development. Achievement of high throughput should be strongly required in the mass production, and to realize this, it is necessary to develop a high power EUV light source or to develop the high sensitive resist. It is effective to achieving high throughput by developing a high sensitive EUV resist, when considering the development situation and the burden of the EUV light source. When a throughput of 80 wafers per hour of a 12-in.-diameter wafer is assumed, and if the sensitivity of the resist is 10 mJ/cm², a source power of 180W is required. If a sensitivity of 5 mJ/cm² is achieved, the required source power is relaxed to be 115W. The origin factor of the sensitivity of an chemically amplified (CA) [2-4] resist are the following matters; 1) the acid generation efficiency, 2) a chemical structure and contents of the photo acid generator (PAG), 3) the activation energy of a deprotection group, 4) the temperature and time of post exposure bake (PEB), 5) the temperature and time of the development.

The many institutes have been researching the affair of 2) to 5), however there are little reports related to 1) and then we focused on 1).

The acid generation mechanism of PAG consists of 2 kinds of processes. One is that the secondary electrons from the base resin generated by EUV exposure make PAG ionization. Another is that the PAG is absorbed EUV light and pass the excitation state [5-9]. Then it is necessary to demonstrate the correlation between the resist absorption and the resist sensitivity, and it is important to obtain the effective atoms and that chemical structures for the high sensitive EUV resist development. Consequently the sensitivities and transmittances of the CA resist including various kinds of PAGs were measured using BL3 and BL10 beamlines in the NewSUBARU synchrotron radiation facility.

2. Experimental Procedure
2.1 Transmission measurement system
The configuration of experimental setup of the transmission measurement system at BL10 beamline is shown in Fig.1. SR light generated from a bending magnet was monochromated by a variable-line-spacing plane grating (VLSPG) to EUV light with a wavelength of 13.5 nm. The wavelength resolution (\(\lambda/\Delta\lambda\)) of the monochromator was approximately 500. A
250-nm-thick silicon filter was installed downstream of the VLSPG, and only the EUV light with a wavelength of 13.5 nm was irradiated to the sample. The pinhole of 1 mm in diameter was installed just before the sample to improve the measurement accuracy, and the light size was controlled smaller than silicon nitride (SiN) membrane size.

Figure 1 shows the configuration of experimental setup of the transmission measurement system at BL10 beamline in NewSUBARU synchrotron radiation facility.

Figure 2 shows the photograph of the transmission measurement tool. The resist sample was set orthogonal to the EUV light axis. The sample position was adjusted relative to the EUV light utilizing x- and y-stages. EUV intensity was measured by a photodiode.

Figure 3 shows the SiN membrane substrate used in this experiment. The sample resist was coated on a 270-nm-thick SiN membrane. The size of silicon substrate is 10 \( \times \) 10 mm\(^2\) and the thickness is 625 \( \mu m \). The membrane window of 2 \( \times \) 2 mm\(^2\) in size is located at the center of the silicon substrate. A 100 nm-thick resist was spin-coated, and prebaked on a hot plate at a temperature of 120°C for 90 s.

The measurement procedure is shown as follows.
(1) SiN membrane substrate was set on the x-y stage in the transmission measurement tool.
(2) Incident EUV light intensity \( I_1 \) was measured without SiN membrane.
(3) EUV light intensity \( I_2 \) was measured through the SiN membrane.
(4) SiN membrane substrate was taken out, resist solution was coated on SiN membrane and this sample was set on the x-y stage.
(5) Incident EUV light intensity \( I_3 \) was measured without the sample.
(6) EUV light intensity \( I_4 \) was measured through the sample.

Finally, each average values such as \( \bar{I}_1 \), \( \bar{I}_2 \), \( \bar{I}_3 \), and \( \bar{I}_4 \) were obtained by 30 measurements. The calculating formula of the transmittance \( T \) of the resist was shown as follows.

\[
T = \frac{\bar{I}_4}{\bar{I}_2/\bar{I}_1}
\]  

2.2 Sensitivity measurement system

The sensitivity experiment was carried out using the resist evaluation system installed at the BL3 of NewSUBARU [10]. The resist evaluation system can simulate a practical exposure spectrum of a six-mirror imaging optics such as \( \alpha \)-demo tool (ASML) and EUV1 (Nikon) exposure tool. Synchrotron light was monochromated to a 13.5 nm wavelength by seven times reflections of a concave mirror and two plane mirrors coated with molybdenum (Mo)/Si multilayer. The intensity of
light was measured at an electron current of a photoelectron when EUV light is irradiated on photoelectric plate. It was converted to the photon number of EUV light. Then, the intensity of light was calculated from the photon number obtained. The resist film thickness was controlled at 100 nm and measured by a multi wavelength interference thickness measurement tool Nanospec model 6100A (NANoMetrics Co. Ltd.). PEB was carried out on a hot plate at the temperature of 90°C for 60 s after the exposure. Aqueous 2.38 wt% of tetra-methyl ammonium hydroxide (TMAH) was used as developer at the temperature of 23°C for 30 s and rinsed with de-ionized water at the temperature of 23°C for 30 s.

2.3 Resist samples

Table 1 shows chemical structure and total atomic absorption cross section (\(\sigma\)) of the resist samples.

Table 1. The chemical structures and total atomic absorption cross section values of each sample

<table>
<thead>
<tr>
<th>sample</th>
<th>polymer</th>
<th>PAG</th>
<th>(\sigma) value of PAG (cm(^2)/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td>(5.07 \times 10^{-17})</td>
</tr>
<tr>
<td>B</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td>(3.34 \times 10^{-17})</td>
</tr>
<tr>
<td>C</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td>(4.02 \times 10^{-17})</td>
</tr>
</tbody>
</table>

This \(\sigma\) vale is used as indication of the transmission and the absorption. If the \(\sigma\) vale is high, it is forecast that the transmission is low. The \(\sigma\) is expressed in the following equation.

\[
\sigma = 2\pi r_0 \lambda f_2
\]  

where \(r_0\) is the classical electron radius (2.82 \(\times\) \(10^{-13}\) cm) and \(\lambda\) is the wavelength and \(f_2\) is the atomic scattering factor [11]. The value of \(\lambda\) is 13.5 nm in this experiment. If the density of a single element and a compound is known, the absorption coefficient and transmission can be forecast from this \(\sigma\). However it is necessary to measure the transmission by using the transmission measurement tool because it is difficult to calculate these values accuracy in the blend material such a resist.

The base polymer was based on the poly-hydroxystyrene system. Propylene glycol monomethylether acetate (PGMEA) was used as the solvent. All cations of the photoacid generator (PAG) employed in this experiment are sulphonium salts, and all anions are sulfonates. The anion of PAG-A is nonafate. The anions of PAG-B and C are benzene sulfonates. The molar ratio between base polymer and PAG were approximately 1:2.7 in mol ratio unit.

3. Results and Discussion

Table 2 shows experimental results of transmittance and sensitivity. The linear absorption coefficient is \(\mu\). The value of \(\mu\) was obtained.

\[
T = \exp(-\mu d)
\]  

where \(d\) is the resist thickness.

Table 2. The experimental results of transmittance and sensitivity

<table>
<thead>
<tr>
<th>sample</th>
<th>(T)</th>
<th>(\mu) ((\mu)m(^{-1}))</th>
<th>(E_0) sensitivity (mJ/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.657</td>
<td>4.20</td>
<td>2.0</td>
</tr>
<tr>
<td>B</td>
<td>0.631</td>
<td>4.60</td>
<td>4.8</td>
</tr>
<tr>
<td>C</td>
<td>0.637</td>
<td>4.51</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The \(E_0\) sensitivities of sample A, B and C were 2.0, 4.8, 4.0 mJ/cm\(^2\), respectively. The liner absorption coefficient of sample A, B, and C were 4.2, 4.6, 4.51 \(\mu m^{-1}\), respectively. A lower liner absorption coefficient value is expected actually because the additive amount of PAG quite more than it is used generally in this experiment. Figure 4(a) shows the relation between the atomic absorption cross section of the cation of PAG and the \(E_0\) sensitivity of each resists. Figure 4(b) shows the relation between the atomic absorption cross section of the anion of PAG and the \(E_0\) sensitivity of each resists.

Larger numbers of the atomic absorption cross
sections of PAG and the anions of PAG have a higher sensitivity. On the other hand, the atomic absorption cross section of the cation of PAG has no relations to the $E_0$ sensitivity. Thus, increasing the absorption of the anion of PAG is very effective for increasing the sensitivity under EUV exposure.

Fig. 4. Correlation of the atomic absorption cross section of (a) cation (b) anion of PAG and $E_0$ sensitivity

Comparing Fig. 4(a) and Fig 4(b), in sensitizing of CA resist, an anion of PAG is more effective rather than a cation of PAG under EUV exposure. As these results, it is assumed that the anion of PAG play an important role in the PAG excitation process instead of secondary electron process. The change of the absorption cross section of the cation of PAG was of little relevance to PAG excitation process. For improving the sensitivity, it is important that the absorption of an anion PAG is increased and the acid generation efficiency is improved. In addition, chemical structure of an anion of PAG has to be designed to take account of the generated acid strength.

4. Conclusion

A transmission measurement system was installed at the BL10 beamline of the NewSUBARU synchrotron facility. We measured the transmittance of a CA resist under EUV exposure and evaluated the relation between the $E_0$ sensitivity and the transmittance of the resist under EUV exposure. Thus, increasing atomic absorption cross section of an anion of PAG is effective in improving the sensitivity of the CA resist in EUVL. However it is not wise to only to choose atoms which have strong photo absorbance because the generated acid strength and efficiency of PAG synthesis have to be taken account to design PAG chemical structure.

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References