Comparison of Resist Outgassing Characterization between High Power EUV and EB

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For high volume manufacturing (HVM) using extreme ultraviolet (EUV) lithography, a practical resist outgassing qualification system is required. Witness sample (WS) testing systems using electron beam (EB) or low power EUV have been proposed as candidate methods, however some issues remain on how these alternative light sources, in comparison to future high power EUV in exposure tools for HVM, will affect actual resist chemical reactions and ultimately resist outgassing. In this paper, we have investigated outgassing from resist induced optics contamination by utilizing two types of WS test systems of high power EUV and EB. A correlation between these light sources is discussed, especially focusing on the resulting chemical phenomena depending on resist material properties.

Keywords: EUV, outgassing, contamination, resist, witness sample

1. Introduction

Extreme ultraviolet (EUV) lithography is the most promising technology for sub-22nm device manufacturing and is on its way to HVM. For these applications, EUV resists are required to have excellent resolution, small line width roughness (LWR), and high sensitivity. The focus on resist material research is on how to concurrently achieve these requirements. However, difficulty is encountered with their reported trade-off relationship [1]. Another potentially significant issue being considered is on how to minimize or avoid outgassing from these resists to prevent possible scanner optics contamination. Thus, there is a need for each of these resists to be screened or qualified before exposure in the scanner.

Numerous resists will need to be tested by the time EUVL reaches HVM stage. Hence, a practical and rapid qualification system which will allow the direct quantification of optics contamination caused by resist outgassing is necessary. Witness sample (WS) testing has been proposed as the strongest candidate in achieving this [2-6].

However, WS testing is not the total solution. Other analysis methods such as quadrupole mass spectrometry (QMS), gas chromatography-mass spectrometry (GC-MS) and pressure-rise tests continue to be applied for the unique advantages they provide [5-9]. For example, GC-MS is the most effective in qualitative analysis of the released resist outgassing species. The QMS and pressure-rise tests are also preferred for their capability in the rapid estimation of resist outgassing. The only disadvantage for these methods is they don’t allow direct analysis of the amount of optics contamination resist outgassing will cause. Thus, these unique testing methods are used complementary to the WS test.

In WS testing, some issues also remain regarding the application of a suitable light source. Ideally, to obtain direct correlation with future HVM scanners, a high power EUV light source is
necessary. However, cost and availability are a critical problem. Thus, EB and low power EUV light sources have been proposed as alternative light sources [2, 3, 5, 6].

It is still unclear how these types of light sources, in comparison to high power EUV, will affect resist chemical reactions and ultimately resist outgassing. To establish a reliable and practical qualification system, further investigations are essential to understand the correlation between high power EUV and these alternatives. In addition, it is important to understand how these types of light sources affect the resulting chemical phenomena depending on resist material.

2. Experimental
2.1. High power EUV based WS testing tool

Figure 1 shows a schematic representation of the High power EUV-based Resist Contamination (HERC) analysis tool [10]. It is setup at the BL9c in the NewSUBARU synchrotron radiation facility, and uses a 10.8m long undulator light source [11]. A Ru (5nm)-capped Mo/Si multilayer mirror is used as WS. The WS is placed facing opposite the resist-coated wafer. Undulator light is reflected on the WS before reaching the wafer coated the resist. At a wavelength of 13.5nm, the illumination intensity is 267mW/cm² on the WS, and 85mW/cm² on the resist surface. The exposure chamber is pumped to ultrahigh vacuum (2~4 x 10⁻⁶ Pa) conditions before exposure, to ensure a clean analysis environment.

Before the contamination growth experiments, the E₀ (dose-to-clear) are measured using the HERC analysis tool and Mark-8 coater / developer with optimum post application bake (PAB) / post exposure bake (PEB) conditions for each resists. After obtaining the E₀, contamination growth experiments are performed by exposing the resist-coated 200mm wafer with 2.5 times the E₀. The total exposed area is equal to one 300mm wafer. During these exposures, pressure increased, to 1~2 x 10⁻⁵ Pa. This was attributed to released resist outgassing.

2.2. EB based WS testing tool

Figure 2 shows a schematic of the EB-based resist contamination analysis tool, the EUVOM-9000 (by Litho Tech Japan). For the irradiation sources, two electron guns at 5 and 0.9 keV was utilized for resist and WS exposure, respectively. The WS for EB system, Ru (50nm) / Si-sub, is positioned alongside of the resist-coated wafer.

For the process flow; the E₀ of each resist (at optimum PAB / PEB conditions) are first evaluated by the EUVOM-9000. Following that, a fresh resist-coated wafer and a cleaned WS are prepared. Then, contamination growth experiments are performed at the measured E₀ dose for a total area equal to a 300mm wafer.

These experiments were done at a base pressure of 2~4 x 10⁻⁶ Pa. During exposure, the base pressure increased to 1~2 x 10⁻⁵ Pa. These measured pressure values were similar to those obtained during experiments at the HERC analysis tool.

The EUVOM-9000 includes a hydrogen-based cleaning unit consisting of a hot-wire filament and a hydrogen gas source. This unit is used to clean carbon-like contaminants on the WS surface before and after the contamination growth exposures.

2.3. Contamination level measurements

The contamination film as deposited are mostly composed of carbon. This is because carbon is major element of the resists analyzed (details in the
next chapter). For this reason, deposited and residual contamination (remaining contaminants after cleaning) are referred to as ‘carbon contamination’.

Carbon contamination levels were determined in the form of contamination thickness as measured by a spectroscopic ellipsometer (SE; M-2000X with focus option by J. A. Woollam). Following the cleaning process, the atomic percentages of residual contaminants were quantified by X-ray photoelectron spectroscopy (XPS).

2.4. Resist materials

Figure 3 summarizes the composition of the model resist samples tested for resist outgassing. Resist platforms such as the polyhydroxystyrene (PHS), methacrylate and PHS-methacrylate hybrid polymer (Hybrid) were selected as the focus of these investigations. Protecting groups employed were chosen in consideration of the polymer platforms. A number of resist samples based on one polymer platform at varied photo acid generator (PAG) cation sizes were also prepared. For the quencher, tri-n-octyl amine was used for all the resist samples.

2.5. Outgassing simulation

Resist outgassing was simulated with DSMC
Neutrals (by Wave Front Co., Ltd.). These simulations were done with base pressure conditions set at $3 \times 10^6$ Pa and the total pressure during outgassing $5 \times 10^5$ Pa. The temperature of the chamber is 23°C. The resist outgassing molecular weight and sticking coefficient was set at realistic values. A relatively higher value for sticking coefficient was set for the WS exposed area compared to un-exposed area.

Figure 4 showed the WS location for these simulations. For case-A, the WS was placed facing opposite the resist-coated wafer, similar to the conditions in the HERC analysis tool. For case-B, the WS was positioned alongside the resist-coated wafer similar to the conditions of the EUVOM-9000.

3. Results and discussion

3.1. Pre-cleaning carbon contamination

3.1.1. Carbon contamination

Before proceeding with discussions on contamination testing results, a correlative investigation between the test tools of HERC analysis tool and EUVOM-9000 was performed. Figure 5 shows the carbon contamination results obtained for five resists using the two analysis tools. Figure 6 shows the correlation between the HERC analysis tool (high power EUV) and EUVOM-9000 (EB) on the carbon contamination results. This graph is a combination of the results as indicated in Fig. 5.

These results confirm a linear correlation between both light sources. This linearity across both zero points was observed in the results estimated based on the exposed resist volume (area $\times$ film-thickness). However, estimations based on exposure time (in which case, the exposed resist volumes are different) did not show good correlation.

Contamination thickness depends on the amount of adhered molecules from resist outgassing on the WS surface. Thus, the volume of exposed resist is considered as one of the most effective factors for understanding the contamination level. Carbon contamination thickness analysis will also show that in evaluating the relative differences between various types of resists or comparing the effect of different types of light sources, it is important to compare results at a fixed volume of exposed resist.

3.1.2. Resist material properties

Carbon contamination was investigated from the viewpoint of the resist material properties. Looking back to Fig. 6, low contamination levels were obtained from the Hybrid-1 polymer resist at both high power EUV and EB light sources. On the other hand, the methacrylate-based resist shows higher contamination level at both light sources. These results were considered to be due to the differences in polarity of these resist materials.

Figure 7 summarizes the polarity trends of the polymer platforms and related de-protected groups. Various compounds are generated in the de-protection reaction. However, for this table, only the assumed major de-protected groups are indicated.

Considering both Fig.6 and Fig.7, results indicate that a low outgassing contamination level is achieved for highly polarized de-protecting groups. This was especially shown by the Hybrid-1 resist which utilizes a highly polarized de-protecting group that includes...
hydroxy-adamantan. Hydroxy-adamantan, when de-protected cannot move freely in the resist film since the polarized species have strong interactions with the polarized regions of polymer matrix. Thus, it is difficult to outgas. In contrast, the adamantylidene de-protected group of Hybrid-3 and methacrylate polymers was easily outgassed because of its poor polarity. This polarity factor in carbon contamination was further confirmed by the relatively low contamination thickness results obtained from the PHS and Hybrid polymers, in comparison to the methacrylate polymer. Both resists include the PHS unit, which is known as the strongest polarized unit.

Figure 8 shows the effect of PAG cation size on carbon contamination as extracted from results in Fig. 5. Contamination level is reduced with larger PAG cation size in both high power EUV and EB experiments. However, this trend was not clearly observed in high power EUV and will require further investigation.

3. 2. Post-cleaning residual contamination

After the cleaning process, the residual contaminants concentrations were analyzed using XPS. Figure 9 shows the detected residual

<table>
<thead>
<tr>
<th>Polymer Platform</th>
<th>De-protected Group</th>
<th>Structure</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid-1</td>
<td>HO</td>
<td></td>
<td>Strong</td>
</tr>
<tr>
<td>PHS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid-3</td>
<td></td>
<td></td>
<td>Poor</td>
</tr>
<tr>
<td>Methacrylate</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Polarity trends of polymer platforms and de-protected groups.

Fig. 8. The effect of PAG cation size on carbon contamination.

Fig. 9. The detected residual elements at high power EUV and EB.
elements in the WS using the CSR001, CSR003, CSR004, and CSR005 at high power EUV and EB. In these results, a similar trend in detected elements was observed for both light sources. No significant difference between high power EUV and EB was found.

Figure 10 shows the detected residual elements in the WS for both exposed and unexposed areas using CSR004 at high power EUV and EB exposures. It is of interest, that in the un-exposed area, a large amount of fluorine was detected only for the samples exposed with EUV. Thus, further investigations were done utilizing time-of-flight secondary ion mass spectrometry (TOF-SIMS) to define the structure of the fluorine containing contaminants detected.

Figure 11 shows TOF-SIMS two dimension (2D)-scan measurement results focused on contaminants with traces of fluorine. C₄F₉SO₃, F and SO₃ were confirmed to have higher fragment intensity in the un-exposed area than at the exposed area using CSR004. These detected compounds come from the PAG anion loaded in the resists analyzed. In the past, the PAG anion has been considered to be a non-outgassing component since they are usually of high molecular weight and are ionized. However, these results show that outgassing from PAG anion also occurs. Moreover, the C₄F₉SO₃ compound is assumed to be mostly outgassing as an acid structure of C₄F₉SO₃H.

Figure 12 shows the TOF-SIMS 2D-scan measurement results focused on C₄F₉SO₃ for the samples analyzed. As shown in the result, C₄F₉SO₃ fragments were detected from all samples. However, this is only true for samples exposed with high power EUV.

As for the question on why these fluorine containing compounds disappeared from the exposed area after cleaning; Fig. 13 shows the proposed schematic model on the mechanism of fluorine containing compounds at the (a) exposed and (b) unexposed areas. There is a high probability that these outgassing PAG anion (fluorine containing) compounds released after exposure adhere to the whole witness sample surface at even concentrations. In the exposed area, these compounds co-exist or are intermixed with easily cleanable carbon contaminants. During the cleaning process, those fluorine containing compounds are cleaned together with these carbon contaminants. On the other hand, in the...
un-exposed area where no carbon contaminants are found, the fluorine containing compounds form strong bonds with the hydrophilic ruthenium surface that was naturally oxidized. Thus, explaining their presence in the un-exposed area even after the cleaning process. Figure 11 and 12 also indicates that no fluorine components were found in the un-exposed area of EB sample.

3.3. Outgassing simulation

To further understand the behavior of fluorine components in resist outgassing, simulation were done on the WS location case-A and B, at high power EUV and EB.

Figure 14 shows the partial pressure distribution of a molecule (M1) of 300 amu molecular weight under the assumption that \( \text{C}_4\text{F}_9\text{SO}_3\text{H} \) is present in the exposure chamber. As a result, the partial pressure on the surface of WS was found to be

![Fig. 12. TOF-SIMS 2D-scan measurement results of C₄F₉SO₃ fragment for CSR001, CSR003, CSR004 and CSR005.](image-url)

![Fig. 13. The proposed schematic model on the mechanism of fluorine containing compounds; (a) exposed area and (b) un-exposed area.](image-url)

![Fig. 14. The partial pressure distribution of M1; (A) similar to the conditions in the HERC analysis tool, (b) similar to the conditions in the EUVOM-9000.](image-url)
higher in case-A compared to that of case-B.

Figure 15 shows the M1 flux at the WS surface for both exposed and un-exposed areas. Based on these results, M1 flux was found to be higher at case-A compared to case-B.

From these outgassing simulations, it was understood that the phenomenon of increased $\text{C}_4\text{F}_9\text{SO}_3\text{H}$ presence at the EUV un-exposed area was not due to the variation in the type of light source, but is more the effect of WS location.

Lastly, based on the outgassing simulations performed, the phenomenon of increased $\text{C}_4\text{F}_9\text{SO}_3\text{H}$ presence at the EUV un-exposed area understood to be mainly due to the effect of WS location. Not the variation in the type of light source, as previously assumed.

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References