Effective EUV Resist Outgassing Barrier Using a Novel Top Coat Material

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The contamination of the EUV optics by resist fragments generated during exposure under high volume manufacturing conditions is a serious threat to the lifetime of the EUV exposure tools. The photon energy of EUV sources largely exceeds the binding energy of all organic molecules and it is known from laser ablation experiments that direct laser induced cleavage of sigma bonds occurs. Even though the fragments formed during the irradiation process are produced in the mid ppb level only, they can act as effective laser deposition precursors and contaminate the tool chamber, the mirrors and the mask.

In this paper, we describe an effective method to eliminate the contamination of EUV optics through the application of a novel outgassing barrier layer (OBL-A) on a conventional ArF resist film, which performs well upon EUV exposure. The outgassing fragments from the resist’s methacrylate resist polymer, its protection groups, the photo acid generator (PAG) and quencher were determined by QMS (quadruple mass spectrometer) with and without application of the OBL-A top barrier layer on the resist film. Results clearly indicate that the outgassing fragments were suppressed effectively which was also verified by the witness plate method. No deposition was observed on the witness mirror using an ellipsometer monitor in real time when applying a top barrier layer on the resist film.

The application of the OBL-A top layer provides an effective means to eliminate the limitations on resist material design as conventional polymers, non-bound PAGs and standard quenchers can be selected for resist design when this novel top barrier layer is applied on the resist film.

Keywords: Photoresist, EUV lithography, outgassing barrier layer, top layer

1. Introduction

Despite a considerable number of technical setbacks in the past, extreme ultraviolet (EUV) lithography [1] is regarded as the main stream technology for the high volume manufacturing (HVM) of critical layers in advanced integrated circuits. One of the issues to overcome is carbon contamination adhesion on the optics and mask inside the EUV exposure tool generated from the organic resist material during EUV exposure.[2] Due to the high energy of EUV photons, resist materials are not only cleaved by default design but can be fragmented via sigma-bond cleavage forming volatile fragments in the vacuum chamber, which condense and densify to intractable residues or films on the mask and mirror system of the EUV tool, thus leading to image distortion and unacceptable loss of irradiation power.

During the last few years numerous studies have improved the understanding about the outgassing phenomena of EUV resists with a focus on qualification, quantification and standard test methodologies [3,4]. Determination of the resist outgassing has been improved especially using Residual Gas Analysis (RGA) and the Witness Sample (WS) method. Currently the major tool manufacturers require the witness sample plate evaluation as the appropriate way to determine if a resist will qualify for practical use [5].

Most EUV resists are chemically derived from DUV resists using chemistries applied in 248 nm and 193 nm lithography. The outgassing of these materials has been controlled to a certain extent by sophisticated design changes of their components, e.g. polymer-bound photo
acid generators (PAG) and quenchers [6], or non-volatile protecting groups. While this usually increases material and manufacturing costs, even those materials produce an unacceptable amount of volatile matter, such as diphenyl sulfide from the PAG [7], which has been identified as one of the major precursors for the contamination of the EUV optics [8]. In addition, serious resist performance degradations, such as insufficient radiation sensitivity, or image degradation due to inadequate diffusion control have been encountered. The appropriate ‘photosensitivity’ of resist materials is of special importance as current EUV sources still lack from sufficient power to enable high-speed and thus cost-effective IC manufacturing with EUV [9].

In this work, the application of a barrier top layer OBL-A on top of the resist to suppress resist outgassing is proposed. From their work with antireflective organic coatings, IC manufacturers are used to apply this simple additional coating step of a top layer, which may not affect the resist performance, but can eliminate the contamination of the EUV exposure tool. The abovementioned analytical methods – i.e. RGA and WS plate testing – have been applied to determine the efficiency of the new top barrier layer OBL-A.

2. Experimental

2.1. High power EUV based WS testing tool

The principle of the high power EUV based resist contamination analysis tool is shown in Fig. 1. An identical setup is used at the BL9C in the NewSUBARU synchrotron radiation facility [8] employing a 10.8-m-long undulator light source. A Ru (5 nm)-capped Mo/Si multilayer mirror is used as WS plate. The WS is placed facing opposite the resist coated wafer. Undulator light is reflected on WS before reaching the resist coated wafer. At a wavelength of 13.5 nm, the illumination intensity is 267 mW/cm² on the WS, and 85 mW/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 and defined analysis environment.

Before the actual contamination measurement the dose to clear (E₀) is determined using the HERC analysis tool and Mark-8 coater / developer with optimum post application bake (PAB) / post exposure bake (PEB) conditions for each wafer. After obtaining the E₀, contamination growth experiments are performed by exposing the resist-coated 200-mm-wafer with 2.5 times the E₀. The total exposed area is equal to that of 300-mm-wafer. During these exposures, an increase of the pressure to 1–2 x 10⁻⁵ Pa is observed, which is attributed to resist outgassing.

A residue gas analysis (RGA) system is also included in this test tool, and the mass of outgassing fragments can be detected by Q-Mass before the WS test. Therefore, it can be determined what kind of outgassing fragments have been generated from either resist or top barrier layer during the exposure process in a ‘one pot’ test.

2.2. Resist material

In order to understand how much the top barrier layer can suppress resist outgas, a conventional (meth)acrylic polymer with an adamantane and an γ-butyl lactone protection groups was selected. As PAG a standard and commercially available triphenyl sulfonium pentafluoroethane salt was used and the quencher was also...
bought from a commercial source.

A mixture of PGME and PGMEA served as the solvents in this resist. The chemical structures of the raw materials are shown in Fig. 2.

2.3. Top barrier layer material

A novel top barrier layer sample, called OBL-A and developed by Merck was used for the experiments.

In pretests, the excellent coating uniformity of OBL-A films on both bare silicon wafers and resist films was confirmed. The wafer coated with OBL-A on bare silicon wafer was developed with 2.38% standard TMAH developer to confirm the solubility of OBL-A in TMAH developer without leaving a residue film.

In order to determine any resist / top barrier layer interactions, the resist was standard baked, overcoated with the OBL-A top coat, dried and then developed with TMAH developer (2.38% in water). The resist film thickness was measured before and after the development process to compare the film thickness change. The result verified that sample with OBL-A barrier coat does not cause significant resist film loss (resist film loss < 2 nm).

2.4. Outgassing test

The resist material was spin coated on 8 inch bare silicon wafers in a TEL Mark8 coater and baked at 120 °C / 90 s. Half of the wafer batch was subsequently overcoated with OBL-A and baked at 95 °C / 60 s.

A resist coated wafer without barrier layer was placed into the exposure chamber of contamination tool BL9C. The outgassing fragments were detected by RGA method before WS testing and the vacuum pressure values were recorded before and after EUV exposure. The Q-mass analysis of the outgassing fragments was done to determine what kind of outgassing fragments generated from the resist (Fig. 3, Table 1). After the Q-mass analysis to determine the outgassing fragments, the wafer was subjected to WS testing. The entire wafer was exposed by EUV light scanning from the wafer center to the edge and at the same time the film thickness of volatile matter generated on WS was measured by an ellipsometer in real time to record how much the film thickness increased on the mirror during wafer exposure.

Table 1. The chemical structure of each mass peak in Fig. 3 was estimated by analyzing to ArF resist components.

<table>
<thead>
<tr>
<th>mass peak</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass number</td>
<td>104</td>
<td>119</td>
<td>162</td>
<td>188</td>
<td>245</td>
</tr>
<tr>
<td>Chemical Structure</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>CF3CF2</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

![Fig. 3. Outgassing fragments of ArF resist were detected by Q-mass of BL09C in NewSUBARU.](image5)
The exposed wafer was developed by TMAH (2.38%) in order to confirm that the wafer has been completely exposed showing no remaining resist residues on the substrate. The same process was applied to a wafer coated with our barrier top layer OBL-A on the resist film.

In order to exclude tool related errors, the outgassing test was repeated at IMEC using the standard witness sample method developed at that location. The IMEC test actually has been qualified by the EUV tool manufacturers. Identical and consistent outgassing results were obtained at both locations.

2.5 Lithographic evaluation

The lithographic performance of the OBL-A barrier layer was evaluated using an ASML NXE:3300 exposure unit to verify its performance impact on EUV resist patterns.

Two pieces of 12-inch-silicon wafers were prepared for this test. Both wafers were treated with HMDS before coating a BARC layer (AZ® EBL92A5, film thickness: 20 nm, Bake: 200 °C), and the EUV resist (Shin-Etsu SEVR-337, film thickness: 50nm, Soft bake: 105 °C, PEB: 95 °C / 60 s) using a TEL clean track ACT 12. One of the two wafers was additionally coated with the top barrier layer OBL-A (film thickness: 30nm, soft bake: 95 °C / 60 s).

Both wafers were exposed under the same exposure conditions to confirm the process window and pattern profile on dose and focus change.

After the exposure process, both wafers were baked at PEB 95 °C/60s and developed using TMAH (2.38%) with a standard development recipe.

3. Results and Discussion

3.1. Outgassing

Resist outgassing fragments as shown in Fig.3 were detected by Q-mass at BL9C at NewSUBARU and the chemical structure of the major mass peaks was assigned to the most likely resist components (Table 1). The peaks a and c result from outgassing of the resist polymer protection groups, peaks b and d were identified as outgassing fragments from the PAG, and peak e can be attributed to a rearrangement product of the quencher.
under EUV irradiation. All of these fragments will contribute to the contamination of mirrors and mask of EUV exposure system.

Fig. 4 shows the mass spectrum of the wafer containing the outgassing barrier layer OBL-A on the resist film. All major peaks of the outgassing fragments shown in Fig. 3 disappeared completely in this chart, indicating that the top barrier layer OBL-A can eliminate the evaporation of volatile resist fragments into the exposure chamber of the EUV tool. The small peaks visible in Fig. 4 were confirmed to be the chamber gassing residues by comparison with a blank test of the exposure chamber. This result proved that OBL-A is effective to cut off resist outgassing.

The efficiency of the outgassing barrier layer OBL-A was also tested using the witness sample (WS) method and the synchrotron EUV exposure system tool BL9C. The result is shown in Fig. 5.

The contamination film thickness on WS plate was measured by an ellipsometer in real time in the period of scanning exposure. Without a barrier layer OBL-A, the outgassing contamination film thickness increased about 9Å after the entire wafer was scanned by EUV light in about 1000 seconds. Upon application of the barrier layer OBL-A, however, the contamination film didn’t increase. This result confirms that OBL-A is very effective to suppress the resist outgassing into the exposure tool chamber as all outgassing fragments can be prevented from resist by this novel top barrier layer.

Consistent outgassing results were obtained at IMEC by the qualified standard WS method too. The result on IMEC EUV resist was shown in Fig. 6, which used the IMEC standard resist (film thickness: 60nm), as the substrate of the top barrier layer OBL-A (film thickness: 30 nm, softbake: 95 °C / 60 s).

EUV tool manufacturers have determined that the acceptable standard threshold of outgassing contamination film increase must be controlled to < 3 nm on WS after exposure of one piece of 300-mm-wafer to qualify the resist material for use in EUV tools [11]. As can be seen, the outgassing of IMEC standard EUV resist

![Graph](image1)

**Table 2: Outgassing Test Results**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Contamination Film Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist</td>
<td>2.4 nm</td>
</tr>
<tr>
<td>OBL-A</td>
<td>0.3 nm</td>
</tr>
<tr>
<td>Resist with OBL-A</td>
<td>0.3 nm</td>
</tr>
</tbody>
</table>

Fig.6. Outgassing tested by standard WS method in imec.

Fig.7. Process window was improved by OBL-A comparing with resist at target size: 29 nm, the gray squares are good area and the black squares are NG.
is in an acceptable level even without use of a barrier layer, however the outgassing film thickness can be further reduced to 0.3 nm when the OBL-A barrier layer is added on the resist film.

According to the outgassing results obtained with the BL09C at NewSUBARU and the qualified standard method at IMEC the contamination from resist outgassing can be cut off completely with the application of the top barrier layer OBL-A. The result indicates that the outgassing issue of any EUV resist can be effectively resolved by this top barrier layer.

### Table 1

<table>
<thead>
<tr>
<th>Dose (mJ/cm²)</th>
<th>Resist</th>
<th>Resist with OBL-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>CD (target: 29 nm)</td>
<td>29.06</td>
<td>29.04</td>
</tr>
<tr>
<td>CDU (sigma)</td>
<td>3.17</td>
<td>2.62</td>
</tr>
<tr>
<td>LWR (nm)</td>
<td>5.33</td>
<td>5.30</td>
</tr>
</tbody>
</table>

![Fig.8. Pattern profile was measured by CD SEM.](image)

3.2. Lithography

It is known that the application of top layers, such as OBL-A, may negatively impact the resist performance with respect to sensitivity, process window or resolution. Certainly, any resist performance degradation is completely unacceptable, in fact it is expected that the application of an additional coating will result in a performance improvement rather than its degradation.

Lithography evaluation was performed using ASML’s NXE:3300 EUV exposure tool with 12-inch-wafer full exposure to compare the performance differences between resist only, and resist with OBL-A barrier coat. The result is depicted in Figure 7. The process window of resist with OBL-A was actually enlarged compared to the resist without OBL-A.

The pattern profile was confirmed by CD SEM, as shown in Figure 8. Application of the barrier coating does not change the CD target size of 29 nm at identical dose, however, both CDU and LWR were improved by OBL-A.

With respect to both process window and pattern profile, the performance was kept or improved once the top barrier layer was used on resist film, and no significant degradation was observed with OBL-A on resist compatibility.

### 4. Conclusion

In this study, the performance benefits of the novel top barrier layer material OBL-A have been discussed. The major target is to resolve the outgassing issue of standard EUV resists. The outgassing from a conventional ArF resist was suppressed effectively when the OBL-A barrier coating was applied as confirmed by both RGA and WS methods in BL09C in NewSUBARU in Spring8. The result was double checked and verified using the qualified standard WS plate method at IMEC, and exposure tests using an ASML EUV exposure tool revealed that the OBL-A overcoat did not deteriorate lithographic performance.

The study further verified that standard DUV polymers, PAGs and quenchers as used in conventional ArF resist can be formulated in EUV resists without the threat of EUV chamber contamination when the barrier layer material OBL-A is applied on the resist film. The need for special resist designs, such as the polymerization of resist components will become obsolete.

**Acknowledgments**

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References