Study of EUV Resist Outgassing/Contamination for Device Integration using EUVL Processes

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EUV lithography is expected to be the main lithography option for sub-22nm device manufacturing. One of the potential issues in EUV photoresist material development is the irradiation induced outgassing of photoresist material and the related risk for optics contamination, especially when the high volume manufacturing tools are introduced. The characterization however of which resist species are important for the contamination, and their quantification, is challenging, since it involves investigation on which parts of the photoresist are outgassing, but also a study of which outgassed species will lead to contamination (and which one will not).

In this paper, we have characterized both the outgassing and the contamination using commercial and model photoresist materials. The outgassing was studied by Residual Gas Analysis (RGA), and indicated that most of the outgassing is related to PAG and protection groups. The contamination was characterized by witness sample testing, and showed that mainly the PAG cation is important for the contamination. Based on this observation several materials were tested with different cation types and loading. This has provided understanding on how to design resist chemistry to minimize the risk of optics contamination in EUV device manufacturing.

Keyword: photoresist, EUV lithography, outgassing, witness sample, contamination

1. Introduction

Resist related outgassing is known to be a potential risk for optics degradation in EUV exposure tools, but its investigation is still very challenging. On one hand side this involves research on how to quantify the resist related outgassing and the contamination, by selection the proper measurement techniques. On the other side, it involves also investigation in the photoresist material composition to identify which part of the resist is most important for the contamination.

To quantify the effect, the first approach is to measure the amount of outgassing of the photoresist under EUV exposure. Residual Gas Analysis (RGA) was found to be a good candidate measurement technique for that, although a careful calibration is required to avoid large differences in measurement results between different test sites [1-3]. In addition, it was found that for a given resist and test set-up, the result can be dependent on the measurement sampling time, the delay between the resist apply and outgas testing, and the exposure parameters [4-6], but taking into account these items, consistent measurement results can be obtained.

Despite the progress in measuring the outgassing in a more accurate way, these techniques still suffer from the uncertainty that part of the resist related outgassing might not contribute to the contamination, and therefore could be ignored. Therefore it has been proposed to use witness sample (WS) testing – i.e. a test where a sample representative for EUV optics is placed in the vicinity of the outgassing resist – to qualify if a resist is a potential risk or not [7]. This method has proven its feasibility, and is currently accepted as the main method for resist qualification for the current full field exposure tools [4-5]. Despite the clear advantage, drawbacks of the technique are that it requires a more complex set-up to generate the contamination on the WS, and that a more complex metrology is required for the analysis of
the WS contamination. In order to simplify this, it has been demonstrated that WS testing is also possible using electron exposure instead of EUV irradiated [6].

On the impact of photoresist chemistry to contamination, much less is reported up to now. Most reporting is related to investigations where photoresist components such as benzene, isobutene, tert-butylbenzene, ..., are leaked to a chamber where WS testing is done at various test conditions [8]. Recently testing at imec and ASML revealed that the photo acid generator (PAG) of the photoresist might be the main contributor to the contamination [6]. This could be a concern for the next-generation EUV exposure tools, since this part of the resist typically contains elements such as sulphur, which are expected to be non-cleanable in these systems.

In this paper, we have characterized both the RGA outgassing and the WS contamination using commercial and model photoresist materials, where mainly the impact of the PAG has been characterized towards contamination. This has provided understanding on how to design resist chemistry to minimize the risk of optics contamination in EUV device manufacturing.

2. Experimental

As indicated above, outgassing and contamination has been investigated at imec by using RGA and WS testing. In this section, the experimental set-up will be outlined, as well as the procedure for RGA and WS test, and the photoresist materials used in testing.

2.1. Imec set-up for RGA and WS testing

This set-up, provided by EUV Technology (Martinez, US), is schematically shown in Fig. 1. It uses an Energetiq EUV source, supplying 10W/2πsr EUV irradiation into the system, which is filtered by a Zr spectral purity filter (SPF). By a multilayer (ML) mirror and grazing incidence mirrors, the EUV irradiation can be applied both on the wafer and on the WS. Spot size on wafer is ~10mm² and the power density is ~4mW/cm². The wafer and the WS can be transferred in and out the sample chamber by respectively an automated wafer load lock and a manual WS load lock. In the chamber a Pfeiffer QMG422 RGA is present to measure the outgassing. The spot size at WS position is much smaller than that at wafer and approximately 1-2mm in diameter. The intensity is measured as Gaussian shaped, with maximum intensity in the spot center of about 80mW/cm². A typical vacuum level that can be obtained in the sample chamber is ~1.5 10⁻⁹mbar.

![Figure 1: schematic representation of the test set-up used for RGA and WS evaluation](image)

2.2. RGA and WS test procedure

The RGA and WS test procedure that was used in the current investigation has been described in more detail in previous papers [4,6]. In order to obtain the resist related impact for RGA outgassing and WS contamination, it was found to be very important that a background (BG) measurement using a Si-wafer was done in addition to the test with resist. The results of this BG can be subtracted from the measurement with the resist coated wafer, in order to obtain the resist related contribution only.

For WS testing, the generated contamination was mainly evaluated by using ellipsometry to measure the maximum thickness of the spot. An example of such a measurement results is shown in Fig. 2, showing the measured thickness profile of the exposed BG and resist contamination spot; the ellipsometer thickness of such a spot is defined as the maximum thickness compared to the region just outside the spot; as can be seen, the resist related thickness is clearly higher than that of the BG.

![Figure 2: Example of WS test result as measured with ellipsometry](image)
2.3. Tested photoresist material samples
In the investigation several commercial resist are evaluated, supplied by five resist vendors. In addition model resist were used, i.e. resists where parts of the chemistry are modified intentionally for this work. More details will be given in the next sections.

3. Interdependence of WS contamination and RGA outgassing and the role of the PAG cation.
3.1. Over-all test results in WS contamination.

As part of the over-all EUV resist evaluation in imec’s EUV lithography program, several resist materials (commercial and model) have been tested by WS, in order to qualify if their use is allowed on the currently installed EUV Alfa Demo Tool from ASML. The criterion to ‘pass’ this test is that the WS contamination thickness should be <1.5 nm. As can be seen from Fig. 3 several resist are meeting this specification, however several from the evaluated samples (mostly model resists) tend to contaminate much more than the specification. Note that the error on the WS contamination result is expected to be around 0.3 nm, so for most resist a significant difference in contamination behavior is observed.

Figure 3: Overview of WS contamination test results obtained in last half year as part of resist outgassing qualification towards ASML ADT.

3.2. Detailed analysis of three photoresist samples.

Since, as expected, the RGA outgassing spectrum was also found to be significantly different for the various resist, a subset of three resists is discussed now towards their outgassing. The description of these three resists is given in Table 1.

Table 1: Description of three resist used for the interdependence of WS results towards RGA outgassing.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist 1</td>
<td>MET-2D (Dow Chemical, exact chemistry unknown)</td>
</tr>
<tr>
<td>Resist 2</td>
<td>Model resist with PHS polymer and triphenyl sulphonium triflate (TPS-OTf) PAG</td>
</tr>
<tr>
<td>Resist 3</td>
<td>Commercial resist (anonymous supplier, exact chemistry unknown, but PAG cation close to TPS, i.e. sulphur containing and similar molecular weight)</td>
</tr>
</tbody>
</table>

The RGA outgassing spectrum of these three resists is shown in Fig. 4 (a-c). Comparing the spectra with mass spectra library data of known chemical species, identification was possible for most of the outgassed material, and therefore estimation for the outgassing of the individual species is also indicated in each graph. Note that the values indicated are not calibrated towards their particular species pumping speed, but nevertheless the outgassing of each species can be compared relatively for the different resists.

For Resist 1, it was found that most of the outgassing is related to isobutene (assumed from protection group), and possibly small traces of tert-butylbenzene (TBB, assumed from PAG), and SO₂ (assumed from PAG), and a low unknown residual. Resist 2 showed overall most outgassing, and resolved mainly isobutene (from protection group), benzene (from PAG cation), diphenyl sulfide (from PAG cation), and again a low residual. Resist 3 showed an overall outgassing comparable to Resist 1, but identification of the species was difficult. Besides a large unknown residual part which is expected to be originated from protection groups, the main identified part was related to the PAG cation, which was indicated to be close to TPS in terms of elements and molecular weight, and from which one of the outgassed elements has a peak close to the main peak of diphenyl sulfide (amu 186).
Figure 4: RGA outgassing characteristics of three resist showing different outgassing behavior. Note that the y-scale in (b) is different for this high outgassing resist.

In Table 2, the contamination results are given for the same three resist, which now can be compared to the interpreted outgassing data. As can be seen the contamination thickness of Resist 1 is very low, while that of Resist 2 and Resist 3 are comparable. Taking all species into account – i.e. over-all outgassing – it was indicated that Resist 1 and Resist 3 were comparable in outgassing, while Resist 2 showed a significantly higher outgassing. This preliminary comparison of three resists therefore already shows that no direct correlation is present between over-all outgassing of all species and the contamination, which suggests that not all species contribute to contamination. From Resist 1 – where mainly isobutene, and traces of TBB and SO2 – it could be conclude that these species have a limited contamination effect, since this resist shows no significant contamination. From Resist 2 – showing mainly isobutene, benzene and diphenyl sulfide – it could be concluded that the observed contamination is due to either benzene or diphenyl sulfide. Since Resist 3 showed in its outgassing spectrum evidence of an outgassing material close to diphenyl sulfide, and had similar contamination results, it was expected that this PAG cation was playing a key role in the contamination. To identify this in more detail, compositional analysis was done on the WS contamination, in order to identify if sulphur is present or not.

Table 2: WS test results of the selected three resists with different outgassing behavior.

<table>
<thead>
<tr>
<th>WS cont. thickness</th>
<th>Resist 1</th>
<th>Resist 2</th>
<th>Resist 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1nm</td>
<td>1.3nm</td>
<td>1.4nm</td>
<td></td>
</tr>
</tbody>
</table>

3.3. Compositional analysis of WS contamination.

In order to have evidence that the sulphur containing PAG cation is playing a key role in the EUV WS contamination, X-ray Photo-electron Spectroscopy (XPS) was performed on the WS contamination spots. Due to sample limitations, only Resist 1 and Resist 3 were analyzed, and in each case both the resist related contamination spot as that of the BG was measured. The results are summarized in Table 3, where only the concentration of C (carbon) and S (sulphur) is indicated, the elements related to the WS stack material are not considered.

As can be seen there is a clear difference between the two resists. For resist 1 no traces are found of S, which confirms that SO2 seems not to contribute to the contamination. Resist 3 on the other hand showed a clear signal for sulphur, which confirms the important role of the sulphur containing PAG cation in the contamination.

Table 3: Compositional analysis by XPS of the WS contamination from Resist 1 and Resist 3.

<table>
<thead>
<tr>
<th></th>
<th>Resist 1</th>
<th>Resist 2</th>
<th>Resist 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>C</td>
<td>100%</td>
<td>100%</td>
<td>98.5%</td>
</tr>
<tr>
<td>S</td>
<td>0%</td>
<td>0%</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

3.4. Over-all interdependence of contamination to outgassing.

Besides the three selected photoresists described below, also the other materials from Fig. 3 that were tested by WS were evaluated towards outgassing. As expected, when the contamination is plotted against total outgassing of all species (Fig. 5), no correlation is found between outgassing and contamination. However for most resists it was found that benzene and diphenyl sulfide were present in the RGA outgassing.
spectrum, which was indicating that most resists had TPS (or a PAG cation close to it) as PAG cation. Since XPS analysis pointed out that the contamination might be related the sulphur containing fragment of the PAG cation (which typically is located in the RGA spectrum around amu 186), the contamination data was plotted now against the outgassing from the amu range 180-190.

Fig. 5 : Contamination versus total outgassing (all species, i.e. amu1-200) confirms that contamination is not correlating with total outgassing.

Fig. 6 : Contamination versus “PAG cation outgassing” (amu180-190) confirms that diphenyl sulfide related PAG cation fragment plays an important role in the contamination for many photoresists from multiple suppliers.

This is shown in Fig. 6, where clearly a correlation is shown for almost all resists taking into account this restricted part of the outgassing. This again confirms that the (sulphur containing) PAG cation is indeed important for the contamination. Moreover it quantifies the relationship, since it indicates that one nanometer of contamination is equivalent to approximately 5e+13 molecules cm\(^{-2}\). Note however that this factor is expected to be system dependent, since the contamination might be dependent on geometrical configuration and exposure spot size on the wafer. Note also that one data point in Fig. 4 is clearly not following the relationship. It is believed that this material has also other species outgassing in the range 180-190, which are not related to contamination.

4. Impact of PAG cation type and loading to contamination.

In addition to the results obtained from our base-line WS qualifications, where the contamination was found to be related to triphenyl sulfonium (TPS) PAG cation (or similar cation), a designed experiment was now done using model resist where the PAG cation type was changed, as well as its loading.

Table 4 : Description of materials tested towards outgassing and contamination as function of PAG type and PAG loading.

<table>
<thead>
<tr>
<th>PAG loading</th>
<th>x0.5eq</th>
<th>x1.0eq</th>
<th>x2.0eq</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="" /></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td><img src="image2" alt="" /></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td><img src="image3" alt="" /></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td><img src="image4" alt="" /></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

4.1 PAG cation types and loading.

The model resist samples for this experiment were supplied by TOK. The samples were based on a methacrylate polymer, where different PAG types were added to in different concentrations as is described in Table 4. As can be seen PAG-A can be considered as a reference since it contains the TPS cation. Compared to PAG-A, two phenyl groups are replaced in PAG-B by two naphtyl groups. In PAG-C and PAG-D, only one phenyl group is replaced by resp. a high molecular weight group R and a tolyl group. In this designed
experiment all different PAG types are evaluated at nominal PAG loading (x1.0eq), while PAG-C is evaluated also at x0.5eq and at x2.0eq.

4.2. Outgassing and contamination results as function of cation type

In Fig. 7-10 results on RGA measurements and WS testing are summarized for the four different PAG materials. In each graph, the RGA spectrum of the material is shown, with a table inset indicating the individual outgassing for the different species (not calibrated), and the WS contamination thickness. As expected for the material with TPS (PAG-A) (Fig. 7), the RGA spectrum shows mainly benzene (main peak at amu78) and diphenyl sulfide (main peak at amu186), but also CO2 related peak is observed (at amu44), which should be related to polymer protection group. The remaining residual outgassing that could not be identified was approximately 5%. As indicated in the inset table the WS contamination thickness of this material was 0.46nm.

(main peak at 236) are introduced in the spectrum. Despite the error on the WS contamination thickness, the impact of changing the PAG from TPS to PAG-B seems a significant decrease in contamination behavior due to this higher molecular weight cation, which is in line with the low outgassing of phenyl naphthyl sulfide (one order of magnitude smaller than the diphenyl sulfide outgassing in the sample with TPS).

Figure 8 : Outgassing and contamination results for sample with PAG-B

The RGA spectrum for the material with PAG-B shows a significantly different behavior for the PAG related fragments (Fig. 8). The benzene peak at amu78 is significantly reduced, since now there is only one (instead of three for TPS) possibility to split off from the PAG-B cation. Moreover, no peak is observed at amu186, since a diphenyl sulfide fragment is not possible here, but instead (small) peaks related to naphtalene (mean peak at amu128) and to phenyl naphthyl sulfide

Figure 9 : Outgassing and contamination results for sample with PAG-C (see text).
4.3. Outgassing and contamination results as function of PAG loading

Finally, with the material with PAG-C, the impact of PAG loading was investigated towards outgassing and contamination. As expected, the RGA spectra are in line with that of Fig. 9, and the results of this could be summarized in Table 5. Overall, an increasing trend of contamination is observed with increasing PAG loading, especially comparing the x1.0eq with x2.0eq. The mismatch between x0.5eq and x1.0eq is expected to be due to the experimental error on the WS contamination thickness measurement, although the diphenyl sulfide outgassing seems to correlate with the measured contamination. This will be further investigated.

Table 5 : Outgassing and contamination results for sample with PAG-C for various PAG loadings.

5. Summary and conclusions

In this paper, we have characterized both the outgassing and the contamination using commercial and model photoresist materials. The outgassing was studied by Residual Gas Analysis (RGA), and indicated that most of the outgassing is related to PAG and protection groups. The contamination was characterized by witness sample (WS) testing, and showed that mainly the sulphur containing PAG cation is important for the contamination. Based on this observation several materials were tested with different cation types and loading. These test suggested that sulfonium based cations with higher molecular weight will result in lower contamination behavior and that contamination is affected by the PAG loading. This has provided understanding on how to design resist chemistry to minimize the risk of optics contamination in EUV device manufacturing.
6. Acknowledgements
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7. References