Assessment of Challenges in EUV Resist Outgassing and Contamination Characterization

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EUV photoresists are considered as a potential source of optics contamination, since they introduce irradiation induced outgassing in the EUV vacuum environment. Therefore before they can be used on the ASML NXE:3100 EUV scanner, the resists need to be tested in dedicated equipment and according to ASML NXE outgas specifications. In line with these guidelines, Imec has been working on the infrastructure set-up to enable the resist outgassing qualification. This infrastructure is based on outgas tool tester which previously has been used for qualifying resists for the ASML ADT, and which has capabilities to do witness sample testing and RGA.

In this paper, we first describe the implementation of the ASML NXE outgas specifications towards the Imec tool infrastructure, and the results obtained on contamination growth of resist related outgassing. In addition the procedure was used to investigate how the change process conditions can impact the contamination qualification result. Finally, preliminary tests were done to compare the qualification results when the photoresist irradiation was changed from EUV exposure to E-gun exposure, which was considered as a more cost-effective solution to use.

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 selecting 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, however differences in test results for different test sites were likely because of differences in the RGA tools, their calibration, and measurement procedure [1-5]. However, its use has been found very important since it has enabled understanding on the kind of outgassing species, and correlation with the resist chemistry [6-9].

Despite these benefits, the resist qualification based on outgassing measurement still suffers 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 [10]. This method has proven its feasibility, and is currently accepted as the main method for resist qualification for exposure tools. At Imec this has been implemented for the ASML Alfa Demo Tool (ADT), and in combination with the RGA more understanding is obtained on the relationship between contamination and resist chemistry [6-9]. For the
ASML NXE:3100 exposure tools, the qualification principle is therefore still used, but refined since the in-situ cleaning techniques of these EUV scanners require to make distinction between cleanable and non-cleanable contamination. These refinements have made the procedure more challenging to establish [11-12].

In this paper, we report on the challenges and the progress to implement the NXE outgassing qualification procedure on the test set-up present at Imec, and describe the results obtained on contamination growth of resist related outgassing. In addition it was investigated how the change process conditions can impact the contamination qualification result. Finally preliminary tests were done to compare the qualification results when the photoresist irradiation is changed from EUV exposure to E-gun exposure, which is considered as a more cost-effective solution to use in the future.

2. Experimental

As described above, ASML has specified a test protocol for qualifying photoresists before these materials can be used in their NXE EUV scanners [11]. In this protocol different subsystems are required as part of outgas test infrastructure to perform the following subsequent steps:

- Contamination growth (CG) in a system tester which enables the generation of contamination on a WS in the vicinity of the outgassing photoresist exposed by EUV or E-gun at dose-to-clear;
- Measurement of total contamination film thickness on WS by spectroscopic ellipsometry;
- Cleaning of contamination by filament H-radicals;
- Measurement of non-cleaned contamination by X-ray photoelectron spectroscopy (XPS).

For the different subsystems, specifications and test criteria need to be achieved [11]. A description of these subsystems at Imec is given below.

2.1. CG tester

The CG tester is based on an tool set-up of EUV Technology (Martinez, US), used for earlier photoresist outgassing testing for the ASML ADT, and upgraded for performance according to the NXE outgassing protocol. A picture and its scheme of current operation is shown in Fig. 1.

To expose the wafer an Energetiq EUV source is integrated, supplying 10W/2msr 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 narrowband EUV irradiation can be applied to the resist coated wafer. Spot size on wafer is \( \sim 20 \text{mm}^2 \) and the power density is \( \sim 4 \text{mW/cm}^2 \). Note that the grazing incidence mirror closest to the wafer acts as a detector (photo-electric effect), therefore the system enables continuous in-situ measurement of the exposed EUV intensity on the wafer.

![Figure 1](a) picture of CG tester as installed at Imec; (b) schematic representation of its operation for RGA and WS testing.

For the exposure of the WS, it was chosen to use an electron gun (Kimball Physics e-gun) at rather low electron energy (200eV) but at high emission current to enable contamination limited regime in a small exposure spot (\( \sim 2-3 \text{mm} \) diameter). The (200mm) wafers and the (1") WS can be transferred in and out the sample chamber by respectively a wafer load lock and a WS load lock. In the chamber a Pfeiffer QMG422 RGA is present to measure the outgassing.

As will be discussed below, the CG tester has also the ability to expose the resist by electron gun, as a way to compare the outgassing and contamination between EUV and e-gun. For this a Kimball Physics e-gun was installed operated at
high electron energy (2keV). In order to have precise dose control, a pulse generator is was added to the power supply.

2.2. Other subsystems
For the measurement of the CG film thickness a KLA-Tencor UV1280 is used. In order to handle the 1” WS substrates in this 200mm wafer tool a pocket-wafer approach was introduced. The filament based hydrogen radical cleaner was supplied by EUV Technology and recently installed at Imec (Fig. 2). For the testing described below, it was mainly used for pre-cleaning. Measurement of the non-cleanable contamination by XPS can be done at Imec using Theta300 (Thermo Instruments). Resist coat and development required for testing is done on TEL ACT8, and resist film thickness (FT) measurement by KLA-Tencor F5.

![Image](image1)

Figure 2: WS hydrogen radical cleaner installed at Imec.

3. CG test procedure at imec and results
Given the experimental set-up described above, the CG test procedure to qualify a photoresist on outgassing in line with the ASML specifications, is done in the following steps.

3.1. Determination of dose-to-clear $E_0$
Since according the protocol the CG test on WS is to be done with the resist exposed at dose-to-clear, this dose $E_0$ is to be determined first for the investigated resist. The standard way to determine the $E_0$ is to use the CG tester in a static step-and-expose modus where at different locations the exposure time is varied by a mechanical shutter. During this exposure, the EUV intensity is constant (and monitored by the integrated detector). A typical result after resist development of this exposure sequence is shown in Fig. 3(a). By the ellipsometry measurement of the remaining resist FT in the center of each spot, the resist contrast curve can be obtained, where then the $E_0$ is defined at the extrapolated line of resp. 80% and 20% of resist film (Fig. 3(b)).

![Image](image2)

Figure 3: (a) picture of processed $E_0$ wafer in step and expose mode; (b) Resulting contrast curve measured with ellipsometry.

![Image](image3)

Figure 4: (a) picture of processed $E_0$ wafer in intensity line scan mode; (b) Resulting contrast curve measured with ellipsometry.

An alternative way to determine the $E_0$ is in scanned intensity mode. In this mode resist wafer is exposed at same scan speed at will be done in the subsequent WS test, while increasing the intensity of the EUV on the Energetiq source. This is illustrated in Fig. 4 (a), where this exposure sequence is shown after resist development, and where from top to bottom the intensity is gradually increased (in the horizontal scanning the intensity is constant). Similarly as in the first method, the resist contrast curve can then be determined by ellipsometry measurement of the resist FT across a line from top to bottom. As is illustrated in Fig. 4(b) this gives very similar shape as obtained by the step and expose mode (Fig. 3(b)). This method has the advantage that it is more directly linked to the WS test, but the limited number of data points (~14 in this case) is a disadvantage. Since with the EUV exposure the two methods can be calibrated towards each other, we currently prefer to use the step-and-repeat method.
3.2. CG WS test procedure.

Since the CG WS tester described earlier can only handle 200mm wafers and the XY stages for exposure scanning had a limited range of 14cm in X and Y, the resulting exposure area on one wafer (∼200cm²) is limited compared to the ASML recommended 300mm wafer area (∼700cm²). Therefore it was agreed that in the Imec WS test two wafers would be included, each exposed during 30min, resulting that then in total ∼400cm² resist area is exposed during the 1hr exposure on the WS, which is required in the protocol. It was found the extra time required to load the second wafer was limited to ∼20% of total CG test time. Moreover, in the test results the loading of the extra wafer did not reveal any extra source of variability. As indicated before, during exposure of both wafers the intensity of the EUV source was set according the $E_0$ dose requirement.

3.3. CG test results

Amongst many other requirements, the main requirements on the CG tester and its results can be summarized in the following:

- CG film thickness (FT) must be in contamination limited regime: this has been tested with two resists (low and high outgassing) at different WS E-gun emission currents, varying from 25μA to 100μA. It has been found that the CG peak film thickness for each resist was at a stable plateau in the region 50μA-100μA. Moreover the thickness profiles of the contamination had a flat top in the central region of the spot, which proves a contamination saturation (intensity profile of E-gun emission current shows Gaussian shaped peaks). 100μA was chosen as set point.

- CG FT must be repeatable: this has been tested using a standard resist, where three CG tests per day were done during 3 days. The test results are illustrated in Fig. 5, showing that a repeatability is obtained of ∼8% (<10% ASML specification).

- Background (BG) CG FT should be low: this has been checked by using bare Si wafers instead of resist coated wafers in the WS test. It was found that the CG FT was ∼0.12nm, which is below ASML spec of 0.3nm, and well below the typical resist related results as illustrated in Fig. 5.

From these test results, it was found that the CG test performance is sufficiently controlled to be used to check the impact of resist and process parameters on resist outgassing qualifications as will be described below.

4. Impact of resist process conditions on CG qualification results.

When a photoresist is used in a lithography production process, it will be typically used at the softbake and post-exposure bake process conditions recommended by the resist supplier, however it is possible that the customer prefers to use it at an offset condition because of specific advantages. Moreover, the customer can use another resist film thickness than the 60nm thickness used in the resist outgas qualification, and also the process for resist adhesion promotion (i.e. priming) might be different. Since the impact of these changes to outgassing and contamination was unknown, dedicated tests were done in the framework of this paper, to anticipate on possible changes in qualification results.

4.1. Photoresist priming.

Photoresist priming is a process step that can be applied prior to coating to promote the adhesion of the photoresist to the underlying substrate. This is in particular important when small features need to be defined on the wafer, since these are most sensitive for adhesion failure. For applying resist on Si-wafers or equivalent materials typically hexamethyl disilazane (HMDS) is used.

In the test protocol for outgassing qualification, HMDS priming is essentially not required since the outgassing tests are done on blanket resist films, and for $E_0$ tests only macroscopic features are defined (like illustrated in Fig. 3(a) and 4(a)). Since the lithography steps on the EUV scanner might use priming or other adhesion promoter, the impact of priming has been investigated here.

In this investigation two resists were evaluated, Resist1 and Resist2, both with and without HMDS priming. It has been found that the impact of
priming on the dose-to-clear can be very significant. In both cases, more resist thickness loss was observed at significantly lower doses in case of no prime, and possible adhesion failure was changing the footing of the contrast curve just above \( E_0 \). The results on \( E_0 \) and contamination in the WS test are summarized in Table 1. As can be seen, both the \( E_0 \) as the CG FT are affected significantly by the priming step. Part of the difference in CG FT can be assigned to the difference in dose, however it is believed that the chemical change of priming can result also in modified outgassing behavior, since dedicated experiments at fixed dose still reveal a difference. In additional experiments – e.g. resist exposures with e-gun as will be discussed later on – it is experienced that WS test results are more stable when using priming (in particular the \( E_0 \) determination), therefore the presence of this step seems important in the outgas qualification. Moreover, preliminary tests using underlayer material in between the photoresist and substrate (which is typically the case in a production process), showed that \( E_0 \) and WS FT results on such layers are typically closer to the test results using resist on Si with priming.

Table 1: Impact of priming on the dose-to-clear and the WS contamination.

<table>
<thead>
<tr>
<th>( E_0 ) (mJ/cm(^2))</th>
<th>No prime</th>
<th>Prime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist1</td>
<td>5.0</td>
<td>7.1</td>
</tr>
<tr>
<td>Resist2</td>
<td>7.3</td>
<td>9.4</td>
</tr>
<tr>
<td>CG FT (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resist1</td>
<td>0.83</td>
<td>1.10</td>
</tr>
<tr>
<td>Resist2</td>
<td>1.83</td>
<td>2.49</td>
</tr>
</tbody>
</table>

4.2. Softbake.

The softbake (SB) of a resist is done after resist coating to remove the solvents from the layer and to result in a chemically stable film for being exposed. Related to the chemistry, the resist supplier will typically recommend at bake temperature, but the end user might prefer to use it at other setting. In order to investigate a possible impact of resist outgassing qualification, WS tests were done using a different resist (Resist3) at various SB temperatures.

Test conditions and results for Resist3 are shown in Table 2. The nominal SB temperature of 100°C was compared to 90°C and 110°C. As can be seen in Table 2, the impact of these changes was very minor both to the \( E_0 \) and the CG FT. Therefore it is believed that such changes in SB do not affect significantly the resist chemistry and therefore also its outgassing behavior. This has been verified with the RGA measurements done during the WS test, where no significant differences are seen amongst the different bakes.

<table>
<thead>
<tr>
<th>SB temperature (°C)</th>
<th>( E_0 ) (mJ/cm(^2))</th>
<th>CG FT (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>7.3</td>
<td>1.78</td>
</tr>
<tr>
<td>100</td>
<td>7.4</td>
<td>1.77</td>
</tr>
<tr>
<td>110</td>
<td>7.3</td>
<td>1.85</td>
</tr>
</tbody>
</table>

4.3. Post-exposure bake.

It is known that the post-exposure bake (PEB) in a lithography step is done after exposure to increase the acid concentration of a chemically amplified resist. This increase is higher when applying a higher PEB temperature, therefore it is expected that when changing the PEB the dose will be affected significantly and therefore also the WS test result.

Table 2: Impact of softbake on dose-to-clear and WS contamination.

<table>
<thead>
<tr>
<th>PEB temperature (°C)</th>
<th>( E_0 ) (mJ/cm(^2))</th>
<th>CG FT (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>11.5</td>
<td>2.42</td>
</tr>
<tr>
<td>90</td>
<td>7.0</td>
<td>1.82</td>
</tr>
<tr>
<td>100</td>
<td>5.5</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The impact has been evaluated again with Resist3, and results are summarized in Table 3. The nominal PEB of 90°C was varied from 80°C to 100°C, and as expected the \( E_0 \) is changing significantly by that. In particular the decrease in PEB, which results in lower chemical amplification, can lead to significantly higher WS contamination. Note that this testing is all done after identical SB (but at different dose, as required in the protocol), therefore the chemical composition of the resist should be identical in the three cases, the only difference is resist exposure at different dose. Therefore it could be expected that the CG FT results have a relationship with the \( E_0 \) results. As can be seen in the correlation plot of Fig. 6, indeed a quasi-linear relationship is found. It is expected that this relationship can be used to predict the WS test result when a resist, qualified at one particular PEB temperature, is used at another PEB temperature, by the \( E_0 \) determination only.
Figure 6: Correlation of CG FT and $E_0$ at different PEB temperatures.

4.4. Resist film thickness.

As indicated in the NXE outgas protocol, the resist film thickness (FT) to use in this testing is 60nm. However, it is very likely that at the customer user a significantly different FT is used, either for imaging reasons or for etching. Therefore it was found important to check the impact of resist thickness variations on the WS test result.

The impact has been evaluated again with Resist3, and results are summarized in Table 4. The nominal resist FT of 60nm was varied from 40nm to 80nm. As can be seen, the $E_0$ is gradually increasing with FT, which could be expected. However this increasing dose and increasing material volume is only giving a moderate increase in CG FT. Therefore it is believed that the contamination is not a pure bulk effect, and that the majority of the outgassing species that contribute to the contamination are originated mainly from the top part of the resist (prior work indicated the species have high atomic masses [6]). This needs further work to investigate.

Table 4: Impact of resist FT on dose-to-clear and WS contamination.

<table>
<thead>
<tr>
<th>Resist FT (nm)</th>
<th>$E_0$ (mJ/cm²)</th>
<th>CG FT (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>5.8</td>
<td>1.72</td>
</tr>
<tr>
<td>60</td>
<td>7.4</td>
<td>1.83</td>
</tr>
<tr>
<td>80</td>
<td>8.1</td>
<td>2.00</td>
</tr>
</tbody>
</table>

5. Comparison of WS test results of EUV and E-gun resist exposure.

As indicated above, the CG tester at imec has an E-gun in the set-up that can expose the photoresist instead of EUV, therefore the outgassing and contamination can be compared in a detailed way for the two exposure modes.

5.1. $E_0$ comparison.

In order to compare the resist outgassing and contamination of the two exposure modes, a detailed benchmarking was done to expose as similar as possible. First the focus voltage of the E-gun is set up in such a way that the exposure spot size of the e-gun is similar to that of the EUV beam, resulting then in an wafer pattern in scanned exposures after development similar to EUV (cf. Fig. 4(a)). As indicated above, it was also found important to introduce a pulse generator for precise dose control, since the emission current of the continuous e-gun exposure is typically much higher than the dose-to-clear. By changing the pulse width at fixed pulse frequency, it was found that the dose could be varied easily and in a controlled way, even for resists with a wide range of sensitivity.

Figure 7: Comparison of resist contrast curve for EUV and E-gun exposure for Resist1 (a) and Resist2 (b).

After this optimization, Resist1 and Resist2 have been compared towards differences in contrast curve and dose-to-clear. Since the dose units for EUV and E-gun are different (mJ/cm² and μC/cm²), the EUV and E-gun contrast curve have been evaluated using an normalized dose (giving value of 1 when the resist FT is at half max thickness). This comparison is shown in Fig. 7 (a) for Resist1, confirming the good correlation of the contrast curve for the two exposure modes. A small difference is seen at the FT at low dose, where the E-gun gives less resist thickness loss than EUV. It is not fully clear if this difference is significant. The normalized plot of contrast curves for Resist2 is shown in Fig. 7 (b). Again the curves are matching well, and now a similar resist thickness behavior is found at low doses. In Table 5, the $E_0$ determined from the contrast curves are shown. As can be seen, the relative difference in $E_0$ for the two resist exposed by EUV is rather large (~30%), while for E-gun this is much smaller (~10%). This limited correlation has also been observed elsewhere [13], and is believed to be related to differences in resist chemistry platform.
5.2. Comparison of CG test results.

Using the determined dose-to-clear values as indicated in Table 5, the CG of Resist1 and Resist2 have been compared between the two exposure modes by WS test. These preliminary results are also summarized in Table 5. It shows that the CG FT results with E-gun are lower for both resists. However, despite the limited correlation of the $E_0$ for the two resists, the CG FT seem to correlate now well: the CG FT for Resist1 is about 45% of that of Resist2 for the two exposure modes. This suggests that the WS test results for EUV and E-gun can be calibrated towards each other.

Table 5: Impact of EUV versus E-gun exposure on the resist dose-to-clear and the WS contamination.

<table>
<thead>
<tr>
<th>$E_0$ (EUV: mJ/cm$^2$) (E-gun: µC/cm$^2$)</th>
<th>EUV</th>
<th>E-gun</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resist1</strong></td>
<td>7.1</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Resist2</strong></td>
<td>9.4</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>CG FT (nm)</strong></td>
<td>1.10</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Resist2</strong></td>
<td>2.49</td>
<td>1.75</td>
</tr>
</tbody>
</table>

6. Summary and conclusions

In this paper, we have described the implementation of the ASML’s specifications on NXE outgas qualification towards the Imec tool infrastructure. It was found that the contamination growth using the procedure was very repeatable with a low background contamination. In addition, the procedure was used to investigate how the change of resist processing conditions could impact the contamination qualification result. Firstly, it was found that the use of resist priming was important in the procedure, to compare the result to other substrate conditions and exposure modes. The impact of softbake and resist thickness was limited, but a change of PEB can have a significant impact through the dose. Finally, preliminary tests were done to compare EUV versus E-gun exposure on the resist. For the two resists investigated, it was found that contrast curve behavior was very similar, however no clear correlation was found for the dose-to-clear. A lower contamination growth was found for E-gun exposure, however in first approximation both witness sample results correlate.

7. Acknowledgements

The author wants to thank R. Perera, and D. Houser from EUV Technology for helpful discussions and support towards the outgas qualification infrastructure. Moreover the photoresist material suppliers – in particular TOK, JSR, Shin-Etsu, and Fujifilm Electronic Materials – are greatly acknowledged for helpful discussion and contribution to this work. Finally the authors would like to thank S. Van Pham, J. Massier, and N. Harned for the collaboration towards the NXE outgas qualification.

8. References

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