Progress Towards Production Worthy EUV Photoresists: Balancing Litho, Outgassing and OOB Performance

James Cameron*, James Thackeray*, Vipul Jain*, Paul LaBeaume*, Suzanne Coley*, Owendi Ongaya*, Mike Wagner* and John Biafore*

*Dow Electronic Materials, 455 Forest St, Marlborough, MA 01752 USA
bKLA-Tencor Division 8843 N. Capital of Texas Highway Austin, TX
jcameron@dow.com

Implementation of EUV Lithography (EUVL) for device high volume manufacturing (HVM) requires advanced photoresists capable of meeting the criteria of advanced logic and memory design rules. To achieve the level of performance required, resists must show excellent performance in terms of resolution, LWR (or CDU) and sensitivity. In addition, resists must meet the outgassing criteria required for HVM on the NXE toolset. Lastly, it is anticipated that resists with low OOB sensitivity will also be required.

In this paper, we describe our progress in all of these areas. Based on our results, we believe we are on track to deliver production worthy resists for the EUVL era.

Keywords: EUVL, EUV, RLS, RCS, resist, mottling, outgassing, OOB

1. Introduction

Extreme Ultra-Violet Lithography (EUVL) is considered the next lithographic patterning technology to extend device scaling beyond ArFi multiple patterning schemes.[1] EUV patterning is attractive as it offers a single exposure pathway to continue scaling. Single exposure schemes with EUVL are anticipated to offer a better Cost of Ownership (COO) proposition than multiple patterning.[2,3] For example, in logic designs, EUVL is expected to be able to significantly reduce the number of cut masks required.[4]

While EUV technology promises many advantages there are three key areas which need to be addressed for EUVL to be ready in time for HVM.[1] The first issue which needs to be overcome is the current low source power which translates into limited throughput.[5] Secondly, concerns over mask blank defectivity need to be resolved.[6] The next issue which needs to be addressed relates to resist materials. In this category, resist suppliers must address three critical areas. The most challenging problem for resist suppliers is the Resolution - Linewidth Roughness - Sensitivity (RLS) tradeoff for line space (L/S) patterns (Fig. 1).

The RLS tradeoff for L/S patterns has been known for several years and continues to be challenging.[7] Recently, the corresponding RCS relationship for contact holes (C/H) where LWR is replaced with the critical dimension uniformity (CDU) term has received a lot of attention.[8,9]

The next materials related issue is outgassing. Up until recently, the specification set by ASML for the NXE3300 was < 3nm carbon growth (CG) for cleanable contamination and < 0.16% (dR/R) reflectivity loss for non-cleanable contamination.[10] Of these two metrics, the cleanable test has proved to be particularly challenging. The initial challenge was the general lack of capacity as test sites struggled to get certified and thereafter had difficulty to
remain certified. More recently, Round Robin testing involving outgas testing of select vendors’ resists at certified tests sites has demonstrated poor correlation among resist test sites.[11,12] For these reasons outgas testing has been a significant challenge from the time the NXE3100 pre-production tool was launched until earlier this year. For example, as of late February 2014, the success rate for meeting the cleanable contamination specification (across all four test sites) was only about 75%.[12] In contrast, no resist has been reported to even come close to failing the non-cleanable portion of the outgassing test.[12]

That being said, ASML recently relaxed the CG specification to < 10nm.[13] The primary reason for relaxing the CG specification is that EUV exposure itself has been found to cause in-situ cleaning thereby allowing the specification to become less aggressive. A potential benefit of relaxing the specification is that it may open up more material options for resist vendors to address the omnipresent RLS and RCS issues.[14]

The last area to address from the resist material side is OOB performance. Unlike prior KrF and ArF scanners, the NXE EUV tool has a non-monochromatic light source. A significant amount of light is emitted from approximately 14nm up until about 300nm. This long wavelength light competes with the desired EUV light at 13.4nm to activate the resist culminating in poor pattern fidelity.[15]

In the recent past we have reported on progress in the following areas: EUV polymer synthesis,[16] EUV sensitization,[17] CDU-sensitivity improvement,[9] leaving group design[18] and molecular resists.[19] In this paper, we will update on our progress in the critical area of RLS and RCS performance. We will explain how we have used a combination of simulation, fundamental resist characterization and experimentation to develop improved resists for both L/S and C/H patterning. We will also update on our progress in development of low outgassing resists based on the ASML’s original 3nm CG specification. Lastly, we will discuss recent results in improving out of band performance.

2. Experimental

2.1 Resist formulations

Various polymers were formulated for positive tone EUV lithographic evaluation at following sites: Albany eMET (AMET), LBNL eMET (BMET) and IMEC (NXE3100). The resist materials were all based on low diffusion chemically amplified resist materials.[20]

2.2 Resist Processing

Resist formulations were spun cast to a resist thickness of 60nm on Si wafers coated with 25nm of underlayer. For high resolution tests, the resists were coated to 30nm film thickness. The films were post-apply baked at 110°C or 130°C for 90 seconds and exposed to a EUV light source as described in Section 2.1. An open frame array was used to generate contrast curves. Patterns were generated using a dark field mask with L/S or C/H patterns. The exposed wafers were post exposure baked at 100°C for 60 seconds and then developed with 0.26N tetramethylammonium hydroxide (TMAH) solution for 30 seconds. Annular exposure conditions were typically used but dipole exposure was used for ultimate resolution. At LBNL, a pseudo PSM was used for high resolution testing.

2.3 Dissolution Rate Testing

Dissolution rates (DR) were analyzed using a LithoTech Japan (LTJ) ARM 800 tool.[21] The resist was spin coated on 60nm AR9™-600 to a resist film thickness of 80nm. Post apply bake was performed at 110°C/90seconds followed by 248nm exposure (Canon ES4/TEL ACT 8 cluster) using the 470nm pattern which exposes 18 channels in the center of the wafer. Each of the 18 channels was radiated with different energies starting at 0mJ/cm² up to 4 times the 248nm E₀ dose. The exposure was done in duplicate. The first wafer was developed on the TEL track. The film thicknesses (measured by Thermawave) in the 18 channels were recorded after PEB and develop. The second wafer was developed in the DR tool for 180 seconds. The dissolution rate was calculated by monitoring the variation in interference of 470nm wavelength light reflected from the substrate and the resist film surface as resist dissolves in the developer using Leapset software from LTJ.

2.4 Out of Band (OOB) Radiation Testing

Out of band (OOB) evaluations were performed by exposing the resist to EUV light (BMET), 193nm light (ASML 5500/1100 0.75NA ArF scanner) and 248nm (Canon ES4 0.80NA KrF scanner). Contrast curves were generated and
the $E_0$ for the various exposure sources was measured. The ratio of $E_0$ (EUV, ArF or KrF) of the new PAG vs. a triphenylsulfonium (TPS) reference was calculated. Further tests were done at LBNL for patterned wafers with and without OOB contamination.[22]

2.5 Witness Plate Outgas Testing

Witness plate outgas testing was performed at three different sites which are all officially qualified for ASML’s outgas test but have three different exposure configurations. The different configurations at the sites used are summarized in Table 1. In addition, these test sites also differ in terms of working distance, sample orientation and temperature control among other things.[12]

<table>
<thead>
<tr>
<th>Test Site</th>
<th>Resist Exposure</th>
<th>Witness Plate Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EUV</td>
<td>EUV</td>
</tr>
<tr>
<td>2</td>
<td>EUV</td>
<td>e-Beam</td>
</tr>
<tr>
<td>3</td>
<td>e-Beam</td>
<td>e-Beam</td>
</tr>
</tbody>
</table>

Table 1. Outgas test site configurations.

3. Results and Discussion

3.1 Addressing RLS Tradeoff Property

Relative to KrF and ArF lithography, EUV has its own unique challenge which is related to the limited number of photons available per unit volume. The photon concentration is so low that there is significant noise in the exposure step especially at the aggressive dose targets required for HVM. This variation in dose is called photon shot noise and has significant ramifications on resist performance.[23] For example, with only a limited number of photons available all resist processes including acid generation,[24] deblocking and development[25] all become subject to significant statistical variation. These statistical variations are at the root of the RLS (and RCS) tradeoff as illustrated in Fig. 2.[26]

In our L/S resist development research activities we have noticed a somewhat unusual failure mode whereby the lines become increasingly mottled as the resolution limit is approached. In this context, mottling is defined as thickness variations in the unexposed line. In the most extreme cases, the resist line may be broken (or pinched) as shown in for Resist A in Fig. 3.

3.2 Resist Mottling and RLS Improvements

Some potential reasons for mottling have been proposed. These include optical or chemical flare leading to random photoacid generation in the unexposed pattern which leads to resist deprotection and partial development of the resist lines. Optical flare is a possibility as there is likely both in-wavelength DC flare and OOB radiation flare during EUV exposure. Given the fact that the mottling signature is random, there is a possibility that there is also stochastic contribution.

In prior CA resist technology (248 and 193nm), chemical flare was identified as the culprit for an unusual resist defect signature where the unexposed resist showed “mouse bites” taken from the surface.[27] In this case, it was postulated that the photoacid was volatilized during PEB and was randomly deposited in the unexposed areas leading to localized thickness loss during PEB and develop. In the case of low diffusion EUV resists it seems unlikely that this mechanism is at play since large, bulky photoacids are typically used to control diffusion for sub 20nm patterning. For example, polymer bound PAG based EUV resists where the photoacid is bound to the polymer would seem particularly unlikely to suffer from this type of chemical flare. This would suggest optical flare from a combination of in-wavelength DC flare and OOB radiation flare may be the most likely cause of mottling.
In pursuit of addressing the RLS tradeoff property, we have recently focused on the mottling issue which is limiting resolution. To this end, we have designed new resists with targeted dissolution properties. Through judicious polymer design, we have been able to systematically vary $R_{\text{max}}$, the maximum dissolution rate of the fully exposed resist, $R_{\text{min}}$, the minimum dissolution rate of the unexposed resist, and $n$, the developer selectivity of the resist material. These polymers were used to experimentally assess mottling behavior as a function of dissolution properties.

In addition, using our Prolith EUV stochastic resist model (SRM) we simulated the effect of varying these dissolution parameters on LWR and LER. Also, given the importance of diffusion control in high resolution lithography we also simulated the impact of diffusion on LWR and LER. The SRM is based on NXE3100 lithographic data and as such we believe this model is readily capable of predicting lithographic performance as a function of varying lithographic parameters within Prolith. In the stochastic resist model, we varied the range of $R_{\text{max}}$, $R_{\text{min}}$, $n$ and acid diffusion length, DL. The range for $R_{\text{max}}$ was varied from 50nm/s to 8000nm/s. The $R_{\text{min}}$ was varied from 0.0005nm/s to 0.1nm/s. Developer selectivity, $n$, was varied from 8 to 40. The acid diffusion length, DL, was varied from 1nm to 5.5nm. It is important to note that the range of simulated model parameters used is representative of resist parameters which we can achieve experimentally. The model predicted low $R_{\text{max}}$ and low $R_{\text{min}}$ would lead to low LWR and LER with $R_{\text{min}}$ showing a stronger response. Developer selectivity, $n$, was anticipated to have a particularly strong effect on LWR and LER with high $n$ being desirable. Increased acid diffusion length was predicted to improve LWR and LER but the effect is rather weak (Fig. 4).

With the simulation results in hand, we next moved to lithographic screening of a range of materials which fit into the modeled parameter space. DR behavior of several modeled resist was characterized. The DR behavior of three of the most interesting resists is shown in Fig. 5. We focused on a material set in which $R_{\text{max}}$ was varied as follows: Resist D ($R_{\text{max}}$ Nominally = 1), Resist C (Relative $R_{\text{max}}$ = 8) and Resist B (Relative $R_{\text{max}}$ = 41). Developer selectivity $n$ was varied across the material space as follows: Resist D ($R_{\text{min}}$ Nominally = 1), Resist C (Relative $R_{\text{min}}$ = 1.9) and Resist B (Relative $R_{\text{min}}$ = 2.1). $R_{\text{min}}$ was held relatively constant in this study (Table 2).

The results of lithographic screening of these resists are also included in Table 2. Relative to Resist D, Resist B shows particularly bad mottling. This resist has the highest $R_{\text{max}}$ and the highest $n$. Based on the model, $R_{\text{max}}$ should negatively impact LWR/LER and high $n$ should improve LWR/LER. Considering this resist shows such poor LWR, it seems that $R_{\text{max}}$ may be more significant than the model predicts (Fig. 4).

![Fig. 5. DRM curves for Resists B, C and D.](image)

<table>
<thead>
<tr>
<th>DR Property</th>
<th>Resist B</th>
<th>Resist C</th>
<th>Resist D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{max}}$ (Normalized)</td>
<td>41</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>$R_{\text{min}}$ (Normalized)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$n$ (Normalized)</td>
<td>2.1</td>
<td>1.9</td>
<td>1</td>
</tr>
</tbody>
</table>

![Table 2. DR and litho data on Resists B, C and D.](image)
In contrast, Resist C with 5 times lower \( R_{\text{max}} \) and similar \( n \) to Resist B showed significantly improved performance. Given resists B and C have similar \( n \), it suggests the performance difference may indeed be due to the lower \( R_{\text{max}} \) in Resist C. This is consistent with the improved LWR with Resist D where \( R_{\text{max}} \) is approximately 40 times lower than Resist B and 8 times lower than Resist C. Based on these results, \( R_{\text{max}} \) appears to be a significant contributor to mottling. We believe this result is due to in-wavelength DC flare and OOB flare causing a small amount of acid to be generated in the unexposed region. In the case of a low \( R_{\text{max}} \) resist, this trace amount of acid would likely only lead to a limited change in DR and therefore minimal thickness change along the unexposed resist. In the case of a high \( R_{\text{max}} \) resist, the small amount of acid generated from optical flare would cause a more substantial change in DR along the resist line which would lead to a more substantial post develop thickness change along the resist line as shown in Fig. 3.

It should be noted that these are our initial results in this area and we will continue to probe mottling using a combination of simulation and experimental screening. Two other metrics which we intend to probe in detail are \( R_{\text{min}} \) and diffusion length as initial simulation indicated these parameters may also contribute to mottling. Indeed, other researchers have recently suggested acid diffusion is a significant contributor to mottling.[28] Another consideration in understanding mottling is the impact of potential variation in the local concentrations of polymer leaving groups, photoacid generators and quenchers. These variations in combination with optical flare could further contribute to the apparent random nature of mottling.

![Fig. 6. 22nm L/S Performance of Resist E at IMEC.](image)

Based on the learnings from our work on mottling, we have developed new resists which show good pattern fidelity as shown for Resist E in Fig. 6. This resist is based on the low \( R_{\text{max}} \) concept described herein coupled with some of our other novel approaches discussed previously.[9,16-18]

### 3.3 Improvements in RCS Tradeoff Property

We have applied a similar combination of simulation and experimentation to drive improvements in C/H resist design. Using this approach we have successfully made significant inroads in addressing the CDU-sensitivity tradeoff. Table 3 illustrates recent progress in developing an advanced C/H resist with good performance at 26nm hp and extendibility to 24nm hp on the NXE3100 scanner. This example is noteworthy as it shows it is possible to simultaneously improve both CDU and sensitivity. This result clearly indicates that it is possible to defeat the RCS tradeoff by judicious resist design. Progress in this area is valuable as performance at these design rules is needed now to enable device makers to benchmark EUVL vs. ArFi through early integration studies.[4,29]

Table 3. Improved C/H RCS performance with Resist G vs. Resist F (Ref.) at IMEC.

<table>
<thead>
<tr>
<th>26nm Top Down View</th>
<th>Resist F</th>
<th>Resist G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Es ( \text{mJ/cm}^2 )</td>
<td>33</td>
<td>26.6 (19% Improvement)</td>
</tr>
<tr>
<td>LCDU (1(\sigma))</td>
<td>1.3</td>
<td>1.1 (15% Improvement)</td>
</tr>
<tr>
<td>CER (3(\sigma))</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>DoF @ 10% EL</td>
<td>300nm</td>
<td>310nm</td>
</tr>
<tr>
<td>Max EL (%)@ Max DoF</td>
<td>15.5@300nm</td>
<td>18.1@310nm</td>
</tr>
</tbody>
</table>

Table 4. 20nm Resolution capability of Resist H at BMET.

<table>
<thead>
<tr>
<th>24nm</th>
<th>22nm</th>
<th>20nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Down View (10%) Mask Bias</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Es (\text{mJ/cm}^2)</td>
<td>47.3</td>
<td>51.1</td>
</tr>
<tr>
<td>DoF 10 CD (nm)</td>
<td>375</td>
<td>322</td>
</tr>
<tr>
<td>EL @ ±100nm DoF (%)</td>
<td>20.4</td>
<td>16.7</td>
</tr>
</tbody>
</table>
Furthermore, with a view to targeting designs where EUVL will likely be implemented for HVM, we routinely evaluate the resolution capability of our resists. Table 4 shows resolution down to 20nm with one of our new high resolution resists, Resist H.

3.4 Resist Outgassing Performance for NXE Usage

Another area of concern in EUV resist design is outgassing. This has been challenging for two reasons. Firstly, the infrastructure was not available to support the learning’s resist vendors need to understand material contributions to outgassing. Secondly, over time it has become clear that there is a strong test site to site variation which in a worst case scenario can mean a resist passes at one site but fails at another. [11,12]

Since the NXE3100 tools were introduced we have had a strong emphasis on designing low outgassing resists. Fig. 7 shows the cleanable outgas test results at Site 1 which uses both EUV exposure on the resist and the witness plate. Under these conditions, we routinely pass the WP cleanables test.

On the other hand, outgassing results from Site 2 show some early samples failing the CG test (Fig. 8). However, over time we successfully designed resists which were capable of passing the cleanable test at this site. For reference, this test site uses EUV exposure on the resist and e-beam exposure on the witness plate.

Lastly, using our low outgas design concepts we were able to routinely pass outgas testing at Site 3 (Fig. 9) which uses the most aggressive configuration with e-beam exposure on both the resist and witness plate.

It should be pointed out that the WP data presented above does not include test results of the same resist at multiple sites. This kind of Round Robin testing has been coordinated by the International EUV Initiative (IEUVI) and results have been shared at the last two IEUVI TWG meetings.[11,12] Our conclusion from the Round Robin tests to date is that there are significant variations in CG measurement and possibly sensitivity too. Clearly, these issues with outgas testing need to be addressed in the near term.

Upon reviewing our cleanable outgas data, it is clear that the vast majority of resists pass the cleanable test. Now with ASML relaxing the specification, we anticipate no issues with cleanable contamination going forward.

In terms of the non-cleanable part of the outgas test, we have never had a resist fail which is consistent with the cumulated data from the IEUVI organization.[11,12]

3.5 OOB Performance

Sensitivity to out of band radiation has previously been shown to negatively impact lithographic performance.[15] As the NXE3300 tool enters the market it is critical to have resists available with low out of band sensitivity to support EUV process development. For OOB improvement, we have focused on PAG optimization as this is the light sensitive component in the photoresist. The results of OOB testing of our new PAGs are summarized in Fig. 10. In this area, we have developed novel PAGs which show comparable EUV sensitivity to
a TPS PAG as used in early EUV resists. However, these novel PAGs show significantly reduced sensitivity at both 193nm and 248nm. In comparison to a TPS PAG, our first generation PAG is 1.9 and 6.2 times less sensitive at 193nm and 248nm respectively. Further optimization led to our second generation PAG, in which we further reduced the 193nm and 248nm sensitivity by factors of 2.7 and 11.6 respectively.

![Graph showing Eo at 13.4, 193 and 248nm](image)

**Fig. 10.** Eo and OOB Ratio Data of New PAGs at EUV, 193nm and 248nm.

Next, we validated our low OOB design by evaluating C/H resist performance using the capability to add 193nm, 248nm and broadband OOB exposure at LBNL.[22] As shown in Fig. 11, all three resists showed good performance with EUV exposure only. However, as longer wavelengths were introduced the performance of the TPS based resist quickly deteriorated. This is a result of the TPS PAG being sensitive to these longer wavelengths. Failure was most apparent at 193nm where the TPS PAG is particularly sensitive. In contrast, the new resists with novel low OOB PAGs maintained good pattern fidelity under our aggressive OOB test conditions in which we added 20% doses of 193nm, 248nm and broadband exposure respectively.

**4. Conclusions**

In this paper we review our recent progress in key areas for EUV resist development. Firstly, we show progress in RLS performance of our EUV resists. Specifically, we have focused on addressing the mottling behavior of L/S resists through a combination of simulation and experimentation. Using this approach, we have successfully improved the performance of our L/S platform. The RCS tradeoff for C/H performance was addressed in a similar fashion to the RLS performance. In this case, we demonstrated improved performance in both CDU and sensitivity which suggests it is possible to defeat the RCS tradeoff by judicious resist design.

Next, we reviewed our resist outgas performance at three sites. Considering ASML’s initial 3nm CG specification, we routinely pass at Test Site 1 with an all EUV configuration. In the case of the EUV/e-Beam configuration at Test Site 2, some early samples failed but we successfully redesigned our resists to pass. Using this modified resist design, we routinely pass on the most aggressive e-beam/e-beam test condition at Test Site 3. Going forward with ASML’s new 10nm CG specification in place we do not anticipate any issues with outgassing. In fact, we propose to take advantage of the relaxed specification to explore new materials sets for improved RLS and RCS performance.

In terms of resist improvement the last area we addressed was OOB performance. In this area, we have designed novel PAGs which show good EUV sensitivity but greatly reduced sensitivity to longer wavelengths (193nm and 248nm). From a lithographic perspective, we validated the low

![Graph showing C/H Patterning test results with and without OOB (193nm, 248nm and broadband exposure)](image)

**Fig. 11.** C/H Patterning test results with and without OOB (193nm, 248nm and broadband exposure).
OOB PAG concept in a C/H application. In comparison to a TPS based resist these novel low OOB PAG based resists maintain performance in our aggressive OOB test using 20% doses of 193nm, 248nm and DUV radiation respectively.

In summary, we show how we have made significant improvement in terms of both RLS and RCS challenges. Furthermore, we demonstrate good outgassing performance and low sensitivity to OOB radiation. By delivering this level performance, we clearly demonstrate that we are actively preparing for the advent of the NXE3300 scanners and ultimately EUVL becoming the preferred approach to rival ArF multiple patterning.

Acknowledgements

The authors acknowledge many coworkers at Dow Electronic Materials especially the Metrology and Analytical Teams. The authors express their gratitude to Sematech, LBNL (CXRO) and IMEC for EUV resist exposures.

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