Metal Based Materials for EUV Lithography

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Considering the scenario that polymer-based resists will possibly be struggling to satisfy all performance criteria for high volume manufacturing imposed by high power sources and high-NA imaging, it seemed necessary to introduce new materials for EUV lithography. To that end, nanometer scale metal clusters, originally designed to be building units of a metal-organic framework, were introduced and tested as metal-based resists. In the work herein, we wish to report all the progress that has been achieved in the patterning performance, focusing mainly on 32 nm and 44 nm pitch 1:1 lines and space pattern.

Keywords: EUV, Metal resists, Developer, Underlayers

1. Introduction

Polymer based resists, either CARs or materials that undergo scission mechanism, constitute a major part of the state-of-the-art materials in photolithography. It has always been a concern though, whether new platforms will be required, as we are looking at new dimensions and radiation sources have changed. Entirely new resist platforms which are specially designed for EUV lithographic requirements are highly desirable. The metal cluster resists show promising lithographic performance under EUV radiation, and in addition, their superior etch resistance and extremely small constituent size, provide clear advantages for ultimate resolution patterning [1].

In this work, we wish to report the progress that has been made on this family of metal-based resists; new resists have been formulated and changes have been made in processing and development conditions that have a positive effect on the lithography performance. For first time as well, we are investigating potential underlayers (ULs) and report unbiased line-edge roughness measurements of these metal resists.

2. Experimental

2.1. Materials and exposure conditions

Resists used were a series of Zn metal clusters synthesized with the same method [1], but employing different ligands, named MR-A, MR-B, MR-C, MR-D, MR-E and MR-F. Underlayers used were either carbon based or silicon-based materials, named SOCs and SOGs respectively; UL-A presented herein falls into SOC category while UL-B is SOG. Metal resists were coated using a SCREEN track with nominal thicknesses varying from 35 nm to 20 nm. A 300 mm TEL CLEAN TRACK™ LITHIUS ProZ™ interfaced with the ASML NXE3300B full field EUV scanner was used, and materials have been exposed under the same illumination conditions. The evaluation of metal resists is done by focusing on 32 nm and 44 nm pitch 1:1 lines and space pattern, while pitches in between them have been studied as well.

2.2. Dissolution rate monitor measurements (DRM)

Dissolution rate of resists was measured using an IMEC custom-build DRM tool. Photoresist is coated onto a 300-mm Si wafer above a 1000 nm thermally grown SiO₂ layer followed by a flood exposure with EUV light using an ASML NXE3300B full field EUV scanner. After exposure, the wafer is brought to the DRM tool for dissolution rate measurement; photoresist is put in contact with the developer, while thickness is measured dynamically by reflectometry [2].

2.3. Metrology

Scanning electron microscope metrology with a Hitachi CG6300 tool was used to collect top-down
images and measure line CD, 3σLER, and 3σLWR. Unbiased measurements were done using a MetroLER Fractilia software [3].

2.4. Total electron yield measurements

Total electron yield (TEY) is an experimental technique to evaluate the number of electrons of the electronic cascade produced in a photosensitive layer during exposure to soft X-ray radiation. TEY experiments have been carried out at the BEAR beamline of the Elettra synchrotron (Trieste, Italy). Samples are prepared by spin coating on to a silicon substrate and then placed into a sample holder in an ultra-high vacuum chamber. Top side of the sample is exposed to the light in the range of 70 to 100 eV, while the backside is mounted onto a chuck by an electrically conductive tape. The electrical current flowing from the back of the sample is measured by an amperometer and is equivalent to the total amount of electrons photoemitted from the surface. Hence, TEY is defined as number of electrons emitted per incident photon.

3. Results and discussion

3.1. Total electron yield measurements

When it comes to new potential resists for EUV, a first evaluation for the suitability can be done using TEY measurements. Results for one representative Zn-based resist are shown in Fig. 1.

![Fig. 1. TEY measurement for one representative metal cluster resist that is studied herein.](image)

Since TEY is a kind of metric of the electronic cascade during exposure to EUV, it seems that these clusters can make a “good” EUV resist, compared to literature data [4].

3.2. Development process

One root cause of poor patterning performance of resists can be the development process (Fig. 2). Development process however is quite broad and comprises many parameters that need to be checked. For this purpose, we tried to investigate development process in detail, covering as many different aspects as we could.

3.2.1. Development behavior of new metal cluster resists

Preliminary data based on dissolution rates of unexposed and exposed areas of the very first resists provided by the material supplier had shown that organic solvent A (used as developer), doesn’t give the desired contrast between the two areas. Before yet running into conclusions about the suitability or no of solvent A as developer, we decided to introduce new metal resists and study their dissolution behavior with the same developer A. Resists studied, already mentioned in the experimental part are based on the same cluster’s design. Use of different ligands though in each cluster, can be proven beneficial, since different ligands can impact not only the solubility behavior but also the switching mechanism of these materials under EUV exposure.

![Fig. 2. All six metal cluster resists have been exposed under the same conditions and have shown that they can resolve 16 nm LS. All materials were coated on bare Si.](image)
Using dissolution rate monitor analysis, the development rate of unexposed and exposed films at different doses has been recorded. What is desired to make a “good” resist and give a good patterning result, is a high solubility difference between exposed and unexposed areas (high contrast). Development rates of metal cluster resists and a positive tone development (PTD) CAR resist as well for comparison purposes have been plotted and are shown in Fig. 3. What someone can see is that the “contrast” of the development rates is not that high; at least not as high as the “contrast” given to the CAR resist using the aqueous alkaline developer in that case. Before switching however to another organic developer, we decided to investigate how developer A works at temperatures other than RT.

3.2.2. Effect of developer’s temperature

Tuning the development’s temperature proved to be an interesting technique to optimize e-beam resists process [5] in the past. Hence, since we are using a “non-ideal” developer, it seemed a reasonable exercise to test how metal cluster resists behave, when developed using the same developer, but at different temperatures. Three resists MR-A, MR-B and MR-F were chosen, while temperatures tested were 6, 22 and 48 °C. Previous reports based on e-beam resists showed that the effect of temperature on resists performance is not always straightforward. In some cases, contrast would benefit from low T, while in some cases from high T. It seems also that resists of the same tonality don’t behave in the same way, which makes sense since the mechanism they work at, can be completely different.

The metal clusters herein are negative tone development (NTD) resists; possibly for some of them the mechanism that leads to switching of solubility under EUV, can be even different. We did want to see though if they follow any trend. Three out of six metal clusters were tested. We chose on purpose clusters MR-A and MR-F that are quite similar, and MR-B that probably follows another mechanism under exposure. For all three, it seems that upon increasing temperature, sensitivity gets lower. We do realize that temperature can be an extra knob to tune contrast and sensitivity, but we still need to work more systematically on that, in order to see how we can benefit the maximum from development at different temperatures. We have noticed some pattern collapse under some development conditions, but it is not clear whether is coming from not ideal temperature or just high resist’s thickness, since the nominal thickness used for this series of experiments was 35 nm and as someone can see in the following section resist’s high nominal thickness can be blamed for pattern collapse. Once we figure it out, we will be able to pick the right temperature for development process; either use cold developer for longer time or stick to warm developer that will compromise our sensitivity but will give us an asset in contrast.

Fig. 3. Development rates of metal resists vs. exposure dose, using organic developer A. Positive tone development (PTD) CAR resist has been plotted as well for comparison purposes.

Fig. 4. Patterning performance of metal cluster resists MR-B at 3 different development temperatures. All three metal clusters studied herein show an increase in dose to size (DtS), when temperature goes up.
3.3. Processing conditions

One of the main issues that we had to deal with these metal clusters in the past, was pattern collapse under development. Studies have shown that resists using alkaline aqueous development and subsequent DI water rinse steps, are prone to pattern collapse for aspect ratios above 2.0 for sub-30 nm resist spacing due to a significant decrease of resist mechanical properties and a sharp increase in capillary forces [6]. We are working with NTD resists using an organic developer, but we still see that there is a big improvement on the patterning performance, when we decrease the nominal thickness of the film (Fig. 4). For all six metal resists studied herein, pattern collapse observed at 35 nm nominal thickness can be overcome when we go down to 25 nm, as shown in Fig. 5, while in some of the exposures done, 20 nm nominal thickness has been used giving similar results to 25 nm.

3.4. Underlayers

It has been very well documented that under EUV exposures, the presence of ULs affects significantly the performance of the resists [7]. This is mainly happening due to the fact that very thin photoresists layers are now used; that means that interactions at the interface of resist and UL will have a much larger impact on the photoresist compared to exposures done at other wavelengths. We have tested different SOCs and SOGs as potential ULs for these metal clusters and we are trying to identify possible materials that will help us to enable very high resolutions. In Fig. 6 (a) are shown the 32 nm and 28 nm pitch LS for MR-F on bare Si and 2 different ULs while in Figs. 6 (b) and (c) are reported some unbiased roughness measurements.

Fig. 5. Patterning performance of metal cluster resists MR-B at 3 different nominal thicknesses. The thicker coatings are affected by severe pattern collapse, while the thinner coatings produce standing lines.

Fig. 6. (a) Patterning performance of metal cluster resists MR-F on bare Si and UL-A, UL-B, at two different resolutions (first row at 16nm and second row at14nm respectively), (b, c) power spectral density of the unbiased left edge LWR and LERleft roughness respectively of the same systems, while using PTD CAR resist on organic UL as well.
Table 1. Summarized roughness and dose measurements for MR-F on bare Si, UL-A, UL-B and PTD CAR resist on top of an organic underlayer for comparison purposes.

<table>
<thead>
<tr>
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<th>LWR</th>
<th>LER(leep)</th>
<th>Dose (mJ/cm²)</th>
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<tbody>
<tr>
<td>CAR/Org.UL</td>
<td>2.82</td>
<td>1.95</td>
<td>55</td>
</tr>
<tr>
<td>MR-F/Si</td>
<td>4.44</td>
<td>3.15</td>
<td>74.5</td>
</tr>
<tr>
<td>MR-F/UL-A</td>
<td>4.12</td>
<td>2.94</td>
<td>91</td>
</tr>
<tr>
<td>MR-F/UL-B</td>
<td>4.49</td>
<td>3.11</td>
<td>74.5</td>
</tr>
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4. Conclusion

It’s not clear yet whether traditional polymer-based resists will satisfy all the criteria for next generation of EUV patterning. Even if polymers “make” it, we need to start considering resists that are made of less components; usually high number of components and their random distribution is accompanied by higher defectivity. Metal cluster resists are investigated as alternative solution to the problem. We reported herein the progress that has been made in patterning performance although there is still room for improvement considering that we are working with a developer that doesn’t give the necessary contrast between exposed and unexposed areas.

References