Progress in EUV Underlayer Materials

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EUV lithography continues to be developed as a technology for sub-30nm and especially sub-20nm pattern imaging in the semiconductor industry. To achieve the desired photoresist resolution, line width roughness and sensitivity (RLS) performance for such fine feature patterns, multilayer materials are almost certainly needed to define the overall lithography process. EUV underlayer (EBL) materials with high EUV photon absorption (EPA) unit can improve resist performance in areas such as sensitivity, imaging capability, dissolution contrast, resolution and process window. In this paper, we report more detailed studies on our new generation of EBL materials, showing enhanced integrated EUV performance including reduction of LWR. One advanced EBL material tested has incorporated metal components, and shows sensitivity improvement as well as high etch selectivity, and can be used as hard mask for next generation pattern imaging.

Keywords: EUV, underlayer, LWR, sensitivity, resolution, OOB radiation, etch rate

1. Introduction

Extreme Ultraviolet (EUV) lithography has been utilized to push the feature size to smaller than 22 nm half pitch node in advanced IC technology recently. Development of resist materials that can meet specifications of resolution, line width roughness and sensitivity (RLS) remains as a significant challenge to manufacturing adoption of EUV.\textsuperscript{1,2} It is required that EUV resists should have performance of LWR < 1.8 nm and sensitivity 10-15 MJ at 22 nm HP.\textsuperscript{3} ArF and KrF resists are widely used as EUV resists. When EUV photon energy is absorbed by resist molecules in the polymer matrix, the photo energy is immediately converted to electrochemical kinetic energy and generates secondary electrons. During one of the most important processes for electron energy degradation, the secondary electrons react with PAG to produce photo acid.\textsuperscript{4,5} While many researchers are working on optimization of resist materials including acid generators and polymer platform to enhance the overall EUV performance,\textsuperscript{5-11} it was realized that multilayer materials are one of the most feasible schemes to achieve the required lithography performance for 22 nm HP and beyond.\textsuperscript{2} Several groups have developed underlayer materials that can improve sensitivity, pattern profile and processing in EUV lithography.\textsuperscript{12-16} Our first generation of EUV underlayer materials AZ\textsuperscript{®} EBL are based on polymer matrix with high EUV photon Absorption.\textsuperscript{16} The combination of increased total film absorbance (TFA) and antireflective properties in AZ\textsuperscript{®} EBL underlayers can effectively enhance the overall EUV performances. The EUV lithography on AZ\textsuperscript{®} EBL underlayers has improved sensitivity, imaging capability, dissolution contrast, resolution and process window. AZ\textsuperscript{®} EBL underlayers can also eliminate resist sensitivity to substrate contamination.

In this paper, we report more detailed studies on our EBL materials such as material shelf-life, film thickness effect and resist compatibility. More importantly, we will present our new generation of AZ\textsuperscript{®} EBL underlayers that focus on reduction of LWR and further enhancement of resist sensitivity with increased etch selectivity. One of the root causes of LWR is the OOB band radiation.\textsuperscript{17,18} In addition to high EUV photon absorption (EPA), the new material has increased deep-UV absorption window comparing to the standard AZ\textsuperscript{®} EBL105A material. We also screened various PAG effect in above new compositions and observed PAG E works most efficiently on LWR reduction among all PAGs we studied. To further increase sensitivity and etch selectivity, metal components can be built in the EBL underlayers. All of the performances of the
new generation EBL materials will be compared with AZ® EBL105A materials. The coating defect results of AZ® EBL underlayers will also be discussed.

2. Experimental

2.1 Material synthesis and formulation preparation

The polymers were synthesized at AZ Electronic Materials USA Corp. EUV underlayer AZ® EXP EBL formulations were prepared by mixing appropriate amount of polymers, x-linker and additives in PGMEA/PGME or other safe solvents. The final solutions were filtered through a micro filter with a pore size of 0.2 um.

2.2 Film thickness measurement and evaluations of optical indices (n, k) for AZ® EXP EBL materials

Underlayer solutions were spun on a 200mm Si wafer and baked at 200 °C/60s. The film thicknesses of the underlayer films were measured by a J.A. Woollam® VUV VASE™ Ellipsometer. The results of the real part of refractive index (n) and the imaginary part of refractive index (k) were obtained by simulations of experimental data using J.A. Woollam® VUV VASE™.

2.3 Solvent and developer resistance tests

Underlayer solutions were spin-coated on silicon wafers and baked at 160, 180, and 200 °C/60s, respectively. To test solvent resistance of the films, solvent such as PGMEA/PGME 70/30 or ethyl lactate was dispensed on the silicon wafer coated with underlayer materials. The solvent was removed by nitrogen blowing after 60s. Film integrity was examined visually or by measuring film thickness before and after soaking. To test developer resistance of the film, a drop of AZ® 300 MIF developer was placed on the coated wafer, the wafer was rinsed with water after 60s and dried by nitrogen blow. Film integrity was examined visually or by measuring film thickness before and after soaking.

2.4 Estimation of EUV absorption for polymer materials

Elemental analysis of materials in AZ® EXP EBL formulations was tested and atomic% of each element was obtained. EUV absorption of the material was estimated based on the atom absorption in literature19 and the atom fraction in the material.

2.5 Etch rate test

Formulations were spun-coated on silicon wafers with a film thickness about 300 nm. The coated wafers were baked at 200 °C/60s. All experiments were carried out without patterned resist on top. The etch rates of various materials were measured using the two conditions summarized in Table 1.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>NE-5000N(ULVAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF POWER</td>
<td>500W(ISM)/100W(Bias)</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>CF4=20sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>10Pa</td>
</tr>
<tr>
<td>Etching Time</td>
<td>10sec</td>
</tr>
<tr>
<td>Back He Temp</td>
<td>20°C</td>
</tr>
</tbody>
</table>

2.6 ArF Lithography

Dry lithographic evaluation was done on a Nikon NSR-306D 0.85NA scanner linked to a TEL Clean Track ACT-12. A silicon wafer was coated with underlayer AZ® EXP EBL solution and baked at 200°C for 60 seconds to form a film with optimum film thickness based on simulations of substrate reflectivity under 193 nm exposure. Using AZ® AX2110P photoresist targeting film thickness of 190 nm was coated on top of the cured underlayer and baked at 100°C for 60 seconds. The wafers were then imaged using a 193 nm Nikon 306D exposure tool with a Numerical Aperture (NA) of 0.85, with Y-Dipole Illumination with 0.85 outer sigma and 0.55 inner sigma. The exposed wafers were then baked at 110°C for 60 seconds and developed using AZ® 300MIF developer (TMAH) for 30 seconds. The patterned wafer then was submitted for scanning electron microscope (SEM) study.

2.7 EUV Lithography

EUV exposure was performed using eximer micro-exposure tool (eMET) at SEMATECH at the University of Albany or micro-exposure tool (MET) at Lawrence Berkeley National Laboratory (LBNL). EUV photoresist is coated on top of above underlayer. It is baked and exposed with 0.3 numerical aperture (NA) with
quadrupole or annular illuminations. The MET tool provides a 5x reduction, a 200x 600 um field on wafer plane. After development, the litho performance is evaluated with both CDSEM topdown measurements and cross section pictures taken under an SEM instrument.

2.8 Wafer Defect Test
Materials were coated on Si wafers using a TEL ACT 12 or a TEL Mark 8 CleanTrack. Wafers were also inspected by a Zeiss Axion II Inspection Microscope (Confocal Scan) or by a SEMVision CX Inspection Microscope from Applied Materials. Defect inspection / analysis were done on a KLA 2360 wafer inspection system or a Surfscan 6220 wafer surface analysis system.

3. Results and Discussion
3.1 General properties of EBL materials with high EUV absorption
Comparing to ArF and KrF lithography, EUV 22 nm HP dimension have much higher shot to noise level due to high energy of EUV photon (> 15 times of ArF photon). The high shot to noise creates problems related to low contrast, poor CD uniformity and large LWR. Improvement of resist sensitivity can enhance the pattern image of EUV by using lower exposure energy. AZ® EBL materials mostly are based on polymer matrix containing high EUV photon absorption (EPA) unit which can efficiently absorb and convert EUV photo energy to generate secondary electrons and eventually help produce photo acid in resists. The polymer platform uses AZ’s ArF bottom antireflective coating (BARC) platform. The structure of the polymer is displayed in Figure 1. The high etch rate polymer backbone contains a UV/DUV chromophore, a crosslinker and a strong EUV photon absorption unit. The underlayer coating is a highly crosslinked low sublimation material with strong absorbance in both EUV and DUV region. The EUV absorption of the AZ® EBL underlayer materials can be estimated based on elemental analysis of polymer compounds and the values of atom absorptions per gram in literature. All of AZ® EBL materials have EUV absorption ranging from 1.5/g to 8.0/g (Conventional ArF BARC AZ® ArF-1C5D has a EUV absorption value of ~ 1.2/g). The EBL underlayer can function well with a film thickness as low as 5 nm. For sub-30 nm imaging, the sensitivity of resist can be improved by more than 10% using EBL underlayer instead of conventional ArF BARC. The EBL materials have also demonstrated better performances in resolution, collapse margin, resist compatibility, and substrate sensitivity, etc.

3.2 Resist compatibility on ultra thin EBL films
AZ® EBL materials generally have good compatibility to EUV resists. Several EUV resist have been exposed and patterned on our EBL underlayer. They all show good pattern profile and process window. No significant footing/scum are observed. Figure 2 gives examples of SEVR-139 and EUVJ50 resist profiles on AZ® EBL105A underlayer at 30 nm HP.

AZ® EBL underlayers have good coating qualities on various substrates such as Si, SiO2 and SiON, etc. The film thickness of AZ® EBL underlayer can be as low as 5 nm. The EUV lithography affords resist pattern without footing/scum at under film thickness ranging 5-20 nm. This also indicates that AZ® EBL underlayers provide strong protection to resist and eliminate substrate poisoning. Figure 3 shows the lithography process windows of EUV resists on AZ® EBL105A underlayers with different film thicknesses at 26 nm HP. It indicates that AZ® EBL materials have
similar performances at 10 nm and 5 nm film thickness in terms of CD uniformity and LWR variation through focus.

Figure 3. Comparison of AZ® EBL105A underlayer performances at 10 nm and 5 nm

3.3 Stability studies on EBL materials

Our EBL materials have demonstrated excellent shelf-life performances based on detailed aging studies of AZ® EBL formulations. Table 2 shows part of the LPC and KLA defect measurements of AZ® EBL105A coating 10 at various temperature storages. No significant changes of LPC and defect counts were observed at -20 °C, 5 °C, 25 °C and 40 °C over six months. Similar results were obtained upon shelf-life studies for AZ® EBL105A coating 5, which gives a thinner film thickness.

Table 2. AZ® EBL 105A Shelf-life and doating defect studies data

<table>
<thead>
<tr>
<th>AZ® EBL105A</th>
<th>Initial</th>
<th>2 Weeks</th>
<th>3 Months</th>
<th>6 Months</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPC@0.15 μm (Whit)</td>
<td>2.2</td>
<td>7.7</td>
<td>3.7</td>
<td>1.4</td>
</tr>
<tr>
<td>LPC@0.08 μm (Whit)</td>
<td>1.3</td>
<td>4.9</td>
<td>2.2</td>
<td>1</td>
</tr>
<tr>
<td>LPC@0.2 μm (Whit)</td>
<td>0.6</td>
<td>3.5</td>
<td>1.6</td>
<td>0.7</td>
</tr>
<tr>
<td>LPC@0.3 μm (Whit)</td>
<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>LPC@0.5 μm (Whit)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>KLA Defects@0.2 μm</td>
<td>0.29</td>
<td>0.37</td>
<td>0.36</td>
<td>0.47</td>
</tr>
<tr>
<td>KLA Defects@0.25 μm</td>
<td>0.14</td>
<td>0.21</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>Surfaces</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3.4. Reduction of LWR by Out of Band (OOB) absorption

The EUV exposure source comprises not only the predominant 13.5 nm radiation but also smaller components of out of band (OOB) DUV/UV radiation in the range of 100nm to 400nm. Actually, the current EUV sources without special treatment contain 10-20% of DUV/UV emission. EUV resists are based on ArF or KrF resist platform and they are sensitive to DUV/UV irradiation. EUV multilayer mirrors reflect the OOB radiation from the EUV sources onto the wafer plane, which cause reduced aerial image contrast of EUV resists. The greatest concern of OOB wavelength is in the range of 160 nm to 260 nm based on published work.\textsuperscript{17,18} It is desirable that the underlayer absorbs not only 13.5 nm radiation but also the out of band radiation. An absorptive underlayer should be helpful to reduce the OOB radiation effect on resist and ultimately improve LWR performances. For our first generation of AZ® EBL materials, ArF bottom antireflective coating (BARC) platform are used to reduce substrate reflectivity and enhance EUV imaging performance.\textsuperscript{16} High EUV absorption elements are incorporated in polymer syntheses. However, ArF underlayer materials only have strong absorbance below 210 nm, the OOB radiation at longer wavelength especially from 220 nm – 260 nm have not been absorbed sufficiently. The unabsorbed OOB radiation may still causes imaging problems. The current work increase the OOB absorption window significantly by incorporating polymer components containing KrF chromophore in the novel EBL underlayer composition. Figure 4 gives absorption curves of the ArF underlayer AZ® EBL105A and absorption curves of the KrF polymers added in the underlayer compositions. The k value is the imaginary part of refractive index, which is related to absorption coefficient measured by ellipsometry. Generally, 10-50 wt% of the new component can be mixed in the total solid content. Certainly, the overall performances of the EUV underlayers were also related to KrF polymer structure and crosslinking groups. The change of chemical properties of underlayer is minimal when polymer A was used for blending. Polymer A increases absorption window of AZ® EBL105A beyond 210 nm up to ~260 nm. It covers the critical range of OOB radiation between 220 nm and 260 nm. Polymer B has excellent absorption between 210 nm to 240 nm. Polymer C has strong absorption beyond 240 nm while its absorption in the desirable range of 210 nm to 230 nm is weak. After examination of formulations
containing KrF polymers A, B, and C at similar blending ratio (~20%), it was found that LWR performance was improved from 5.1 nm to 4.8 nm by using AZ® EBL133A material containing polymer A comparing to that of AZ® EBL105A reference. As shown in Figure 5, the X-SEM of pattern profile on AZ® EBL133A underlayer has less footing and scum than that on AZ® EBL105A underlayer. The results of LWR comparisons are also listed in Table 3 in section 3.5.

Figure 4. Absorption curves for films of AZ® EBL105A and KrF polymer A, B, and C measured by ellipsometry

3.5 Reduction of footing/LWR by PAG addition

PAGs in resist materials are critical to photospeed at least since most acid is formed in the exposed part of EUV resist through interaction of secondary electron with PAGs. PAGs were also added in EUV underlayers to improve sensitivity. However, addition of PAGs in EUV underlayers often causes line collapse and line roughness. The overall PAG effects on EUV underlayer performances were not encouraging although slight enhancement of photospeed was observed. It was believed that PAG diffusion from underlayer into resist causes line collapse. We have tried to find PAGs that can not only improve photospeed but also reduce footing and LWR without line collapsing issue. PAGs that have different diffusion rates were studied. It was observed that the less diffusive PAG E has the best performances regarding to footing and LWR reduction. In addition, the collapse margin of resist did not change significantly when PAG E is used. Table 3 has shown the comparison of LWR and DOF results using AZ® EBL105A (no PAG), AZ® EBL133A (no PAG), and AZ® EBL133E (PAG E added) for resist patterning at 27 nm HP.

Table 3. Comparison of LWR and DOF results on AZ® EBL105A, AZ® EBL133A, and AZ® EBL133E underlayers.

<table>
<thead>
<tr>
<th></th>
<th>AZ@EBL105A</th>
<th>AZ@EBL133A</th>
<th>AZ@EBL133E</th>
</tr>
</thead>
<tbody>
<tr>
<td>LWR*(nm)</td>
<td>5.1</td>
<td>4.8</td>
<td>4.6</td>
</tr>
<tr>
<td>DOF(um)</td>
<td>0.13</td>
<td>0.12</td>
<td>0.12</td>
</tr>
</tbody>
</table>

* Long range measurement.

3.6. Improvement of sensitivity and etch selectivity by metallic components.

A spin-on coating material containing metallic components was studied as prospective EUV underlayer materials. Most metals have higher EUV photon absorbance than those of C, H, N, and O elements in organic materials. The electron mobility in a metal containing film should also be better than that in a organic matrix, which may improve quantum yield of acid generation via efficient interaction between secondary electron and PAGs at the resist/underlayer interfaces. It was reported that some metallic underlayer material can improve EUV sensitivity significantly. These metallic underlayers have excellent etch selectivity to assist pattern transfer to substrate. They can be used as a hard mask to replace silicon material in case a trilayer process is needed for sub-20nm HP features. Since high energy source of EUV is one of the root causes of
LWR, the metallic material may potentially improve overall EUV photoresist performance. The material we studied contains substantial amount of metal compounds, which gives significantly higher etch selectivity (8x) than silicon material at oxygen plasma etch conditions, as shown in Figure 6. The etch rate of the metallic underlayer in CF₄ gas is lower than that of the silicon material (1/3). The metallic underlayer has also demonstrated enhanced photosensitivity comparing to organic underlayers. Figure 7 shows that the resist sensitivity improved by ~20% when the metallic underlayer material of AZ® MHM003 was used as EUV underlayers instead of AZ® EBL105A underlayer. Investigation of LWR performance of the metallic underlayer is in process.

### Table 4. Coating defect inspection result of AZ® EBL92A

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>AZ EXP EBL92A Coating 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wafer# 1</td>
<td>020_UV_BF</td>
</tr>
<tr>
<td>Defect Density</td>
<td>0.07</td>
</tr>
<tr>
<td>Wafer# 2</td>
<td>025_V6_BF</td>
</tr>
<tr>
<td>Defect Density</td>
<td>0.04</td>
</tr>
<tr>
<td>Average defect density per cm²</td>
<td>0.09</td>
</tr>
</tbody>
</table>

![Figure 6. Etch rate comparison of metallic and silicon underlayers at CF₄ and O₂ plasma etch conditions.](image)

![Figure 7. Comparison of resist sensitivity on metallic underlayer AZ® MHM003 and AZ® EBL105A underlayer](image)

3.7 Coating defect inspection.

In order to achieve manufacturing-worthy coating defect level, the filtration process was optimized to obtain excellent defect density (defect count) on 8" wafers shown in Table 4 and Figure 8.

Figure 8. Wafer Maps of AZ® EBL92A (defect count and defect density)

4. Conclusions

AZ® EBL underlayers are developed based on high EUV absorption EUV materials. Our EBL materials have shown good shelf-life and excellent resist compatibility. The materials have demonstrated similar performance in a wide range of film thickness (5-20 nm). The new generation of EBL materials, AZ® EBL133A, has improved absorption window of OOB radiation from EUV sources and has enhanced LWR reduction comparing to previous AZ EBL materials. PAG effects on EUV underlayer performances have been investigated and the overall performances of EUV resist can be improved by using AZ® EBL133E underlayer containing a less diffusive PAG E. A new metallic underlayer has been studied in EUV process. It has improved EUV sensitivity and high etch selectivity than silicon materials. The novel EBL materials have shown low defect counts on wafer maps by using KLA 2360 Inspection Parameters. We will continue to work on improvement of EUV underlayer materials as part of the integrated material solution of sub-20nm process using EUV lithography.
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References