Challenges to Overcome Trade-off between High Resolution and High Sensitivity in EUV Lithography

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EUV lithography is one of the most promising candidate technologies for high volume manufacturing (HVM) of 7nm node beyond. To apply EUV lithography to HVM, high resolution and fast sensitivity with low roughness are required. To improve sensitivity, we developed novel PAG that includes electron withdrawing group (EWG). The PAG showed high acid generation efficiency from our experimental results. Increasing proton source unit in resist matrix also produces high acid generation efficiency. By using the novel PAG and increasing proton source unit ratio in resist matrix, we developed novel resists that produces high resolution patterns with reasonable sensitivity.

Keywords: EUV lithography, photoresist, proton source, photo acid generator

1. Introduction

Now semiconductor industry faces issues such as overlay margin, edge placement error and increase manufacturing cost due to the process complication by extending ArF lithography [1]. EUV lithography is expected to be replaced to ArF lithography and solve those issues by its process simplification and resolution [2]. One of the main challenges applying EUV lithography to HVM is throughput. EUV light source has been improved steadily in recent years, but further improvement of the source power is necessary for HVM [3] and also EUV resists which show fast sensitivity are strongly required. It is well known that resolution (R), line width/edge roughness (L) and sensitivity (S) are trade-off relationship [4]. To overcome the trade-off, sensitivity of photoresist need to be improved without degradation of ultimate resolution and roughness. Increasing acid generation efficiency is one of the most important items in order to improve sensitivity without resolution degradation. Acid generation mechanism of CA resists for EUV exposure was reported [5,6]. To increase acid generation efficiency, increasing the reactivity of PAG cation with secondary electron is important and also increasing proton source concentration in resist matrix should be helpful. Controlling acid diffusion during post exposure bake (PEB) is important to improve resolution. Chemical blur produced during PEB is suppressed by decreasing acid diffusion length, but sensitivity is slowed at the same time. To overcome resolution-sensitivity trade-off, increasing acid generation efficiency with suppressing acid diffusion should be needed [7-9].

In this article, we will show experimental results of acid generation efficiency PAG cations measured by acid titration method which coumarin 6 derivative was used as indicator [10]. The effect of proton source unit content for acid generation efficiency is also evaluated. Then resist design for overcoming resolution-sensitivity trade-off...
will be discussed.

2. Experimental

2.1. Resist Materials

Resist materials were prepared by mixing resins, photo acid generator (PAG), quencher and solvents. Resist solutions were passed through 0.25 um PTFE filter before evaluations.

2.2. Contrast curve evaluation

Resist solutions were coated on silicon substrate with hexamethyldisilazane (HMDS) treatment. Coated wafers were baked at 110°C for 60 seconds (PAB) and exposed by EUV light with different energies (0 ~ 24mJ/cm²). Then, post exposure bake (PEB) was conducted at 110°C for 60 seconds. Wafers were developed with a 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution at 23 °C for 60 seconds in the CLEAN TRACK ACT-8 system. Film thickness changes with respect to exposure dose were compared among photoresists.

2.3. Quantum yield measurement

Quantum yields of acid generation were measured by a titration method using Coumarin 6(C6) as an indicator (C6 experiment) [10]. C6 was added to photoresists instead of quencher. Resist solutions were coated on a quartz substrate by spin coating and 1300 nm film thickness films were prepared. Wafers were baked at 90°C for 60 seconds (PAB), and exposed by EUV light with different energies. UV spectra of exposed films were measured to observe absorbance change at specific wavelength by UV absorption spectroscopy (JASCO V-570).

2.4. EUV Lithography

Resist solutions were coated on silicon substrate treated with HMDS or organic under layer with 25nm~45nm film thickness. Coated wafers were baked at each temperature for 60 seconds (PAB), and PEB was conducted at each temperature for 60 seconds. Wafers were exposed by EUV light using ASML NXE3300 installed at IMEC with 0.33 NA or interference lithography tool at Paul Scherrer Institut (PSI) [11]. Resulting wafers were developed with a 2.38% TMAH aqueous solution and a rinse material.

3. Results and Discussion

3.1. Acid generation efficiency

Increasing acid generation efficiency is necessary for current EUV photoresist in order to meet sensitivity requirement for HVM [7]. Increasing reactivity of PAG cation with secondary electron and increasing the number of proton used as an acid should be effective to increase acid generation efficiency. Quantum yield of acid generation was calculated from following equation.

\[ \varphi = \frac{\text{Abs} \times \varepsilon}{\text{Dose} \times \#\text{EUV}} \] (1)

Where \( \varphi \) is a quantum yield of acid generation, Abs (mol\(^{-1}\)Lcm\(^{-1}\)) is film absorption at 563 nm, \( \varepsilon \) (mol\(^{-1}\)Lcm\(^{-1}\)) is an absorption coefficient of C6, Dose (ml/cm²) is EUV exposure energy and \#EUV is number of photons radiated on to resist film.

First, new PAG cations were evaluated. Mainly PAGs are reacted with secondary electron generated by absorbing EUV light in resist matrix. To increase the yield of acid generation, increase the reactivity of PAG cation with secondary electron should be effective.

Fig. 1. Energy potential model of PAG cations having EDG or EWG.

PAG cation having EWG group tends to indicate lower LUMO energy than normal triphenyl sulfonium (TPS) cation (Fig. 1). By attaching the EWG group on TPS cation, the reactivity with electron is expected to be increased. The relationship between acid generation efficiency and LUMO energy was investigated. We prepared two PAG cations. One has a control EWG (EWG1). Another has new EWG (EWG2). LUMO energy was calculated for these two PAGs by Chem3D (using MOPAC PM3) and quantum yields were measured by an acid titration method. Experimental results are put on Figure 2. The cation having EWG2 has lower LUMO energy and higher quantum yield than the cation having EWG1. This result suggests that
electron affinity of PAG cation is increased by lowering LUMO energy and acid generation efficiency is increased by applying EWG on PAG cation.

<table>
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<tr>
<th>PAG Cation</th>
<th>EWG1</th>
<th>EWG2</th>
</tr>
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<tbody>
<tr>
<td>LUMO Energy [eV]</td>
<td>-5.06</td>
<td>-5.37</td>
</tr>
<tr>
<td>ϕ (Quantum yield)</td>
<td>2.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Fig. 2. LUMO energy and Quantum yield comparison. Quantum yield value is the average among different EUV exposure energies (3, 6 and 9 mJcm⁻²)

Next, an ability of proton source unit was investigated. From the view point of acid generation mechanism [5,6], increasing proton source unit in resist matrix should help increasing acid generation efficiency. Quantum yields of two polymers in Figure 3 were measured in order to clarify proton source ability. One polymer has 50% proton source unit, another is homo polymer of proton source. Figure 3 shows the quantum yield of resist films made from each polymer, control PAG and C6. Quantum yield was increased by increasing proton source content in polymer. This result indicates that high proton source unit content in resist matrix helps improvement of acid generation efficiency.

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>Proton source</th>
<th>Protecting group</th>
<th>Proton source</th>
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<tbody>
<tr>
<td></td>
<td>50%</td>
<td>50%</td>
<td>100%</td>
</tr>
<tr>
<td>ϕ (Quantum yield)</td>
<td>2.5</td>
<td>2.9</td>
<td></td>
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</tbody>
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Fig. 3. Quantum yields for polymers with different proton source content. Quantum yield value is the average among different EUV exposure energies (3, 6 and 9 mJ cm⁻²).

3.2. Photoresist development

By taking account of results of previous section, sensitivity can be improved. Next, we focused resolution improvement. To improve resolution, a chemical blur produced by acid diffusion during PEB process need to be suppressed. To decrease acid diffusion length, film Tg is increased by controlling Tg enhancer unit ratio in resist matrix. We checked the optimal ratio of Tg enhancer unit by following experiment to maximize lithographic performance. Samples with different Tg enhancer ratio were prepared and patterned using EB exposure tool (Test-1, 2, 3). Figure 4 shows the differences of samples and results of EB patterning. Tg enhancer ratio was increased from Test-1 by replacing protecting group in resist base polymer for Test-2, 3. As a comparison result, Test-2 showed best performance (resolution) in those three samples. By increasing Tg enhancer unit, resolution was improved for Test-2. But further increase of Tg enhancer (Test-3) didn’t show better performance than Test-2. Protecting group ratio is decreased for Test-3 and it might lead to degradation of chemical contrast. From those results, we found that the optimal Tg enhancer ratio is similar equality with Test-2.

<table>
<thead>
<tr>
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<th>Test-1</th>
<th>Test-2</th>
<th>Test-3</th>
</tr>
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<tbody>
<tr>
<td>Sensitivity (relative)</td>
<td>1.00</td>
<td>1.02</td>
<td>1.06</td>
</tr>
<tr>
<td>Resolution</td>
<td>22nm</td>
<td>20nm</td>
<td>22nm</td>
</tr>
<tr>
<td>Proton source (relative)</td>
<td>1.0eq</td>
<td>1.0eq</td>
<td>1.0eq</td>
</tr>
<tr>
<td>Tg enhancer (relative)</td>
<td>1.0eq</td>
<td>2.0eq</td>
<td>3.0eq</td>
</tr>
<tr>
<td>Protecting group ratio</td>
<td>High</td>
<td>Middle</td>
<td>Low</td>
</tr>
</tbody>
</table>

Fig. 4. Sample differences and EB screening results of Resist D, E, F. Tg enhancer ratio and protecting group ratio are different for each samples. (30, 28, 26, 24, 22, 20nm half pitch, 1:1 LS pattern, 100kV electron beam exposure tool).

In consideration of experimental results in previous section and the EB screening result, a new photoresist was prepared. Figure 5 shows differences of components between Resist A and Resist B (new). Resist B contains 1.34 times higher ratio of proton source unit in base polymer and PAG cation with EWG2 to improve acid generation efficiency. Also Resist B includes higher amount of Tg enhancer unit. By applying units increasing acid generation efficiency and increasing film Tg, resist formulation is optimized to improve both of sensitivity and resolution.
EUV patterning for those two resists were conducted with NXE3300 at IMEC and summarized in Figure 6. In Figure 6, Resist A resolved 14nm half pitch (hp) LS pattern with 38.6 mJ/cm² but doesn't at 13nm hp. On the other hand, Resist B resolved 13 nm hp LS with 43.0mJ/cm² at 14nm LS. In addition, Z-factor [12] of Resist B is lower than Resist A. This indicates that Resist B overcomes RLS trade-off by applying new materials.

Resist C was prepared in the similar concept as Resist B and was evaluated with interference lithography tool at PSI. The result is shown in Figure 7. Resist C resolved 12 nm hp at 36.1 mJ/cm².

Figure 8 shows contrast curves of Resist A and B. In the graph, dissolution at low dose area was suppressed for Resist B and Resist B showed steeper slope than Resist A. It means that dissolution contrast was improved for Resist B by applying new materials.

By applying new PAG cation and controlling Tg of resist matrix, ultimate resolution was improved with no degradation of sensitivity. The improvement is also observed in the contrast curve.

4. Conclusion

New PAG cation having electron withdrawing group is designed to improve sensitivity and acid generation efficiency is measured by acid titration experiment. Also the ability of proton source unit in resist matrix was evaluated. It was found that LUMO energy of PAG cation correlates with quantum yield of acid generation and decreasing LUMO energy is effective to improve sensitivity. Also we have confirmed that increasing proton source unit in resist matrix is effective to improve sensitivity.

New photoresists were prepared to improve sensitivity and ultimate resolution. By applying new PAG cation and controlling proton source ratio in resist matrix, acid generation efficiency was enhanced. At the same time, acid diffusion length was decreased and chemical blur was suppressed by increasing polymer Tg.

As results of EUV patterning for new resists, high resolution patterns were resolved with high sensitivity (13nm LS / 43mJ at imec, 12nm LS / 36.1mJ at PSI). From results of EUV patterning, the effectiveness of material design and photoresist design was confirmed.

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References