Study of PAG Material Design for ArF Immersion Photoresist


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One of some critical issues for ArF immersion lithography was leaching of resist components to water fluid. To decrease the leaching amount, increase hydrophobicity of Photo Acid Generator (PAG) was one of the most effective methods. The hydrophobicity of PAG was detected by simulating Log-P value and measuring Retention Time (RT) on reversed phase chromatography. However, simple high hydrophobic PAG indicated high defect number. The improvement of this issue was achieved by introducing acid cleavable group into PAG cation frame. It may suggest that PAG material proposed on this study showed low leaching amount and low defect risk as new concept for ArF immersion resist.

Keywords: ArF immersion, PAG, hydrophobicity, leaching, defect, acid cleavable group

1. Introduction

The chemically amplified resists are used for wide variety of applications, and manufacturing of 45 nm half-pitch device using immersion ArF lithography system under investigation. Water is the ideal medium for ArF immersion lithography and this water immersion system could reach up to 1.3 numerical aperture (NA), applied higher resolution capability. However, there are some critical issues for a mass production. One of them is leaching of resist components. It has already known that the leaching components into the water as immersion fluid are low molecular compounds like a PAG, photoacids and quencher in the resist film. Those cause a negative impact on lithographic performance of the resist and also damage the lens system, and therefore it should be controlled to decrease the leaching amount. Generally there are two approaches to minimize the leaching amount. One is an application of a topcoat material on the resist film, and the other is non-topcoat approach. The former application is expected to shut off the leaching from the resist film into water fluid by a topcoat as barrier layer in between. However, PAG (or photoacid) could penetrate even through topcoat layer from resist or intermixing layer between their interfaces. These phenomena happened during exposure and successive PEB step. In order to estimate film property and prevent those phenomena, it is considered that Solubility Parameter values of the resist polymer and topcoat polymer are the key parameter. As the later application, some techniques to control lowering leaching amount have been already reported. For example, decrease of the leaching amount

Received November 19, 2008
Accepted December 20, 2008
can be achieved by adding fluorine additives into current resist formulation, and by changing hydrophobicity of PAG\textsuperscript{3-8}. The other side, some papers already reported residue defect occurred due to high hydrophobic resist surface, which is not only ArF dry resist but also immersion resist\textsuperscript{9}. One of the reports explained some types of defect issue (called as development defect) was accelerated by the photo-decomposed material from PAG in alkaline developer\textsuperscript{10}. According to the conclusion of present paper, it is thought that technique for simple high hydrophobic PAG to decrease leaching amount would make defect risk higher.

In this study, we report about the design of PAG that can maintain low leaching amount to water fluid and decrease the defect simultaneously.

2. Experimental

2.1 Materials

ArF model resists were prepared by using adamantane-based acyclic methacrylate ter-polymer, PAG and tertiary amine quencher in mixture of propylene glycol monomethyl ether acetate (PGMEA) and propylene glycol monomethyl ether (PGME). The ter-polymer of model resist is shown in Fig. 1.

Varieties of PAG containing different physico-chemical properties were also used to study the leaching analysis and defect inspection. The chemical structures of these PAGs are shown in Fig. 2.

2.2 Leaching Analysis

The amounts of each PAG were decided as same amount of molar ratio as 3 wt\% of PAG D respectively, as normalized to the polymer weight. All polymer and resist components were dissolved in mixture of PGMEA/PGME and filtered prior to the film preparation. The resist films were prepared on silicon wafers applied hexamethyldisilazane (HMDS) with 90 °C bake for 60 seconds by adjusting the spin speed with a Clean Track ACT-8 manufactured by Tokyo Electron Ltd. The film thickness was adjusted to 250 nm. The post-applied bake (PAB) was operated at 90 °C for 60 seconds.

In extraction step of leaching material from resist, 150 µl de-ionized water was scanned on coated wafers with 12 mm/second scan speed and covering spirally whole wafer and then recovered. Leaching amount of PAG cation and anion were quantified by LC-MS (manufactured by Agilent) system.

2.3 Estimation of PAG hydrophobicity

The hydrophobicity of PAG was evaluated by simulating Log-P value and measuring RT on reversed phase chromatography. Log-P value was simulated and calculated for cation unit of PAG by CAChe Work System (Fujitsu Corporation). RT of each PAG was measured by high performance liquid chromatography (HPLC) manufactured by Waters. HPLC was equipped with the octadecylsilyl column and UV detector (detected wavelength was 210 nm), and eluent was used acetonitrile/H\textsubscript{2}O=60/40 (wt\%).

2.4 Dissolution inhibitor effect

The evaluation resist was prepared by using alkaline developable polymer, each PAGs in mixture of PGMEA / PGME.

Silicon water was applied HMDS with 90 °C bake for 60 seconds. The resist film was formed with 400 nm thicknesses and applied 90 °C prebake for 60 seconds. This wafer was exposed with open frame at ArF dry condition using Nikon NSR-S302B (NA 0.60). Then this wafer
was baked with 100 °C for 60 seconds and developed by 2.38 % tetramethylammonium hydroxide aqueous (TMAH) at 23 °C. Dissolution inhibition effect of each PAG was estimated by measuring the dissolution rate of resist by TMAH.

2.5 Defect Inspection
Defect inspection was evaluated with ArF immersion exposure. The resist solution was filtered and spin-coated on a bottom anti-reflection coating (BARC) prepared on silicon wafer, and prebaked at 115 °C for 60 seconds to give a film thickness of 150 nm with a Clean Track ACT-12 manufactured by Tokyo Electron Ltd. A commercially available product was used for the BARC. After baking, the wafer was exposed by NSR-5609B manufactured by Nikon. Evaluated pattern size was 55 nm Line and Space, and pitch size was 110 nm. Following exposure, wafer was baked with 115 °C for 60 seconds. Then development was done with 2.38 % TMAH. This sample defect count was inspected for defects with KLA2371 manufactured by KLA-Tencor, and defect review was carried out on a SEMVision G3 manufactured by AMAT.

3. Results and Discussion
3.1 Relationship of PAG hydrophobicity and leaching amount
PAGs and their photoacids are recently known for the most critical components that have serious impact in the leaching issue. Therefore, PAGs and their photoacids were evaluated for the leaching analysis in this interfacial mass transfer study. It has been reported that a high molecular weight and bulky structure cation showed low leaching amount. According to this report, hydrophobic characteristic of PAG cation structure was one of the key parameter. To estimate this parameter, simulating Log-P value and measuring RT at reversed phase chromatography were evaluated. Log-P value is a physical properties value, and this value is displayed by equation (1).

\[ \text{Log } P_{\text{ow}} = \text{Log} \frac{[\text{PAG}]_{\text{n-octanol layer}}}{[\text{PAG}]_{\text{H}_2\text{O layer}}} \tag{1} \]

This value of the compounds has been used as a conventional measure of hydrophobicity in general. Log-P value is the distribution ratio of the compound to water/n-octanol phase at equilibrium state. Generally, low Log-P value indicates hydrophilic and high number shows hydrophobic property.

The other side, measuring RT on reversed phase chromatography is very effective method to characterize PAG hydrophobicity. The short retention time indicates hydrophilic, and the long one means hydrophobic property. Table 1 shows these results. As a result, Log-P value and RT obtained a very good correlation. This result suggested that high carbon number and bulky structure showed higher hydrophobicity.

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<th>Table 1. Various parameters for estimation of PAG hydrophobicity</th>
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<tr>
<td>PAG</td>
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<td>Log-P</td>
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<td>RT [minutes]</td>
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Fig. 3 shows Log-P value and leaching amount relationship. Leaching amount was measured by actual PAG in resist film. In this time, nonaflate anion was used. Increase Log-P value indicated less leaching and new designed PAG F has an alicyclic protecting group showed significant improvement.

![Fig. 3. Leaching amount versus Log-P value](image)

3.2 Influence of dissolution inhibition effect to alkaline developer
It was reported that photo-decomposed material from PAG increased defect count in alkaline developer. It is thought that technique for simple high hydrophobic of PAG to decrease leaching amount would make defect risk higher. Therefore, influence of dissolution inhibitor effect to alkaline developer was evaluated using PAG C-F. Fig. 4 shows these results. The
evaluation resist was prepared by using alkaline developable polymer. The dissolution rate to TMAH of resist using only this polymer was ca. 20 Å/second. The dissolution rates of resist using PAG C and PAG D were 30-40 Å/second through exposure dose. This result indicates that PAG C and D were working as dissolution promoter in alkaline developer. On the other hand, the dissolution rate of resist using PAG E that has high hydrophobicity is difficult to change through exposure dose. The value was ca. 8 Å/second, and this result suggests that PAG E has higher dissolution inhibitor effect to alkaline developer than PAG C and D. It is also estimated that PAG F has higher hydrophobic structure than PAG E at un-exposure area. Therefore, the inhibition effect to alkaline developer of PAG F is also larger at non-exposure area (6 Å/second). However, the dissolution rate of PAG F increases as exposure dose increase. This result means that PAG F reacted with the acid generated by the exposure and the de-protecting reaction was occurred. Then PAG G has carboxylic group as dissoluble to alkaline developer is generated (Fig. 5). Therefore, it is expected that resist using PAG F has much higher dissolution promotion effect than the other PAG. Moreover, it is shown that PAG F and G have similar behavior at dissolution rate to alkaline developer. However, the dissolution behavior did not overlapped completely. It is considered that this result shows influence of methylidenediamantane generated with de-protecting reaction.

3.3 Defect inspection of each PAGs with immersion exposure
Defect inspection was evaluated with ArF immersion exposure by using model resists containing each PAG C, D, E, F and G. This result shows Fig. 6, and the pictures of these defect modes show Fig. 7.

As a result, it is understood that blob and residue defect becomes increasing tendency as higher hydrophobicity like PAG C-E. On the other hand, defect count of PAG F showed least number though this PAG has highest hydrophobicity and lowest dissolution rate at non-exposure area in evaluated PAGs. This result means that trade-off between low elution risk and
low defect risk is achieved by introducing the acid cleavable group into PAG cation frame. In addition, the mechanism of PAG photo-decomposed compound is one of most important factors to decrease defect risk.

4. Conclusion
In this paper, new PAG design for ArF immersion resists has been studied in order to maintain low leaching amount to water fluid and decrease the defect simultaneously. From the standpoint of leaching amount decrease, increase hydrophobicity of PAG showed good improvement. General simple high hydrophobic PAG to decrease leaching amount has the risk to increase defect issue. The trade-off relationship was improved by introducing acid cleavable group into PAG cation frame. The mechanism control of the decomposed compounds by photo irradiation is very important, and it seems that it will be necessary to study the influence of this on lithographic and defect performance.

References