Challenges and Progress in Defectivity for Advanced ArF Lithography Process

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1. Introduction

ArF lithography process is still in important position due to the delay of extreme ultraviolet lithography (EUVL). Exposure tools, masks, and resist materials are being developed for EUVL toward 10 nm node generation and beyond. but it has still issues for realizing fundamental semiconductor device production manufacturing.

The contentious challenges in ArF lithography is to reduce cost with multi-pattering process [1].

The two types process of resist are well-known as materials for ArF immersion exposure. One is top coat (TC) process resist and the other is TC-less one [2-5].

Generally, TC-less process has cost advantage compared to TC process.

The present study aims to find various type of polymers design to satisfy both hydrophobic property for high scan speed and low defectivity requirements. For positive-tone development (PTD) by using alkaline developer, the polarity-change property function of film surface from hydrophobic to hydrophilic after alkaline development process is key to reduce defectivity. High alkaline-responsive materials which were not only polymer additives but also copolymers as main component of resist have good potential to defectivity reducing. Additionally, to suppress swelling is one of very impotent factor to improve bridge type defect mode.

Keywords: ArF immersion lithography extension, Chemically amplified resist, Defectivity, Polarity change material

2. Experimental

2.1. Materials
ArF resist compositions used in this study were prepared by dissolving methacrylate copolymer having an acid-decomposable group, photo acid generators (PAG), amines as quencher and hydrophobic polymer additives into organic solvents. The resulting solutions were filtered with 0.01 \( \mu \text{m} \) polyethylene filter for lithography evaluations.

2.2. Defect analysis

Line and space patterns with 100 nm pitch 1:1 duty were printed by NXT1970i (manufactured by ASML) on a 12-inch wafer and inspected. The defect distribution of the wafer was detected with UVision5 (manufactured by AMAT) and the shape of the defects was observed using SEMcisionG4 (manufactured by AMAT).

2.3. QCM measurement

Mass variation of resist film during development step was measured by a quarts crystal microbalance (QCM) method with a Litho Tech Japan QCM QZ-3 system at 23 °C (substrate is 5 MHz quartz resonators with a gold electrodes). In the QCM measurements, a 2.38% TMAH is used as developer to monitor the mass variation of resist coated film (thickness: 100 nm). Average dissolution rates were calculated using a period of time for film clearing. To analyze swelling behavior, QCM data were collected on exposed resist film which was prepared under ArF exposure at the specific dose prior to the QCM measurement.

3. Results and discussion

3.1. Demand to a TC-less resist

In high scan speed immersion lithography, TC-less resist surface should have hydrophobic property, that is, higher RCA (receding contact angle) is required. The scan speed of the latest exposure tools rises in 800 mm/s now [6]. We set more than 85 degree RCA as a target to keep good followability for these exposure tools. TC-less resists which have hydrophobic surface can be obtained by addition of hydrophobic polymers which can localize to resist surface and low surface energy are easy to localize to resist surface [8].

3.2. Comparison of PTD and NTD

The two types of resists are well known as TC-less resist. One is alkaline developer for positive-tone development (PTD) process, the other is organic solvent developer for negative-tone development (NTD) process [7].

TC-less resist should have high hydrophobic property of film surface for high speed scan. In the case of NTD, organic solvent developer has high affinity to hydrophobic resist surface, indicating that fast scan speed and low defectivity, which should be affected by developer wettability, are compatible. On the other hand, in the case of PTD, fast scan speed and low defectivity might be a tradeoff relation because alkaline developer shows low affinity to hydrophobic resist surface as described in Table 1. For PTD process, polarity change polymer additives in development process are well-known as advantage for defectivity [8].

![Table 1. PTD have a concern for defectivity with trade-off relationship between hydrophobic property for high scan and hydrophilic property for defectivity.](image)

Figure 1 shows the behavior of dissolution progress of PTD process, and NTD process.

NTD process gave more smoothly dissolution than PTD process, that is, organic solvent development proceeds simpler salvation. On the other hand, PTD process is more complex to dissolve for developer than NTD process. These phenomena on PTD is explained swelling by acid-base equilibrium reaction between methacrylic and TMA+ is caused, and then, the penetration progresses by alkaline developer into the deprotected resist film [9].

![Fig. 1. PTD process is not easier to dissolve for developer than NTD in behavior through development process.](image)
Additionally, Fig. 2 indicates that PTD process has basically more swelling behavior than NTD process [10]. Swelling causes degradation of pattern roughness after development, so that it might become probable cause of bridge type defect. This should be suppressed for both defectivity and pattern roughness improvement on PTD process.

Fig. 2. Swelling is observed at PTD process in situ high speed-AFM measurement [10].

3.3. Strategy of polarity change for PTD
To satisfy the both hydrophobic property for high scan and hydrophilic property for defectivity, polarity change with alkaline-responsive function was applied to polymer additives and copolymers as Fig. 3. Polymer additives was given the function which is the polarity change of film surface from hydrophobic to hydrophilic after alkaline development process. Furthermore, copolymers should have the suppress of swelling against alkaline developer for smoothly dissolution due to attainment of good defectivity.

Fig. 3. Polarity change materials design additives in alkaline development process were studied copolymers in addition to polymer.

3.4. Investigation of an alkaline-responsive copolymer
For polymer additives design for alkaline-responsive, we selected a linkage group which can be hydrolyzed by alkali-stimulus as an alkaline-responsive polarity change unit. Furthermore, a strong electron withdrawing group (EWG) can accelerate hydrolysis reactivity drastically. From these results, we designed alkaline-responsive polymer additive-A which has middle spacer length with a strong EWG as the optimized structure [8].

This knowledge expands to copolymer design. In result of investigation as Fig. 4, copolymer-A which has spacer linkage group shows low swelling behavior. Swelling have a risk of possible cause for bridge type defect mode with increasing pattern roughness. this effect of alkaline-responsive part is considered that high wettability for alkaline developer is suitable to less swelling.

Fig. 4. Copolymer-A shows less swelling with alkaline-responsive linkage group.

Figure 5 shows defectivity result by using this copolymer-A. The defect counts are reduced compared to conventional one. This is considered that less swelling improves bridge type defect by low affinity to alkaline developer. The results after classified defect mode indicates in Fig. 6. Actually, bridge mode was reduced drastically with the high hydrolysis rate and that is understood the low swelling and good affinity for alkaline developer were increased by high hydrolysis function.

Fig. 5. Low defectivity was showed by using copolymer-A.
Fig. 6. The result of defect counts (a) with classified defect mode such as bridge and residue (b) by using copolymer-A.

Additionally, the combination of polymer additives and copolymers with polarity change function by alkaline-responsive type achieves low defectivity at high speed scan as Table 2. Therefore, the approach with alkaline-responsive design has good potential to reduce defectivity as advanced TC-less resist.

Table 2. The combination of polymer additives and copolymers achieves low defectivity at high speed scan.

<table>
<thead>
<tr>
<th>Polymer additives</th>
<th>Hydrophobic type</th>
<th>Alkaline-responsive type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main polymer</td>
<td>Conventional type</td>
<td>Conventional type</td>
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<tr>
<td>Defect map</td>
<td>RCA 86°</td>
<td>85°</td>
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<tr>
<td></td>
<td>SCA after Dev.</td>
<td>85°</td>
</tr>
<tr>
<td></td>
<td>Defect counts</td>
<td>58600</td>
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</tbody>
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4. Conclusion

Two approaches regarding polarity change type materials in development process were studied for a next generation TC-less resist to meet the demand for fast scan speed and low defectivity.

An alkaline-responsive polymer additive is the best solution and suitable polymer design enabled to achieve high RCA and low SCA after development simultaneously.

Additionally, the copolymer which has high hydrolysis rate for no swelling design shows good potential to defect reduction.

References