Thermal Flow Property for 193nm Photoresist with Low Dispersion Polymer

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For the enhancement of the Lithography Technology, photo-resist performance, especially in base polymer, has important rules. Currently, in ArF lithography, base polymer of poly-acrylate has been widely selected, but the performance especially in contact-hole pattern has very severe limit in process window, such as DOF. In this presentation, by using poly-acrylate polymer, which has fairly good PEB margin and thermal stability, we further studied thermal flow performance of its in different polymer disparity. As the result, we observed that low disparity polymer showed small thermal flow rate and consequently, showed enhancement of common DOF in contact-hole pattern.

Keywords: 193nm lithography, photoresist, controlled radical polymerization, RAFT method, low dispersion polymer, thermal flow process, shrink process

1. Introduction

Recently, the technology development of 65nmNanode process has been discussed in many places. But in this area, ArF resist performance on dry process is nearly the limit. In order to improve it, ArF Immersion, F2 lithography, EUV lithography, and also the other methods are introduced as next potentials. However, due to the availability of the exposure tool or the production through-put, it is true that ArF single layer resist approach on dry is still highly expected to extend the life time.

In the ArF single dry process, it is said that one of the most difficult layer would be contact-hole. This is because exposure for contact-hole pattern requires the dark reticle, which obtains optically small contrast. Moreover, instead of optical contrast, photo-resist must have high resolution contrast for developer between exposed area and unexposed one. It is clear that the contrast requirement is higher than L/S patterning. Also, for contact-hole patterning, in order to increase the resolution(R), it is necessary to increase lens NA(R=λ₀/NA) but on the other hand, DOF becomes smaller based on Reili equation (DOF=k₂λ₀/NA²). Therefore, selection of proper NA is also very important while optimizing resist contrast for total process optimization.

In this, one of the effective approaches to makes 100nm or smaller hole size is thermal flow process, which has been implemented on KrF lithography enhancement and only requires simple process flow, unlike other shrink technology.

In this paper, we would like to discuss the thermal flow process performance with low disparity polymer produced with radical polymerization method.
2. Experimental

2.1 Materials

The low dispersed polymers are all prepared by Union Chemical Laboratory's RAFT polymerization (Living Radical Polymerization). In the experiment, only conventional synthesis method and purification method are used, and all the materials for resist formulation are also using only commercialized materials.

2.2 Characterizations

Purity of the monomers was analyzed on GC instrument (HP 5890B, GC-FID; with Stabilwax fused silica capillary column, OD .53mm x 30m). 1H NMR (1H; 200MHz) was obtained on Bruker AC-200 instrument. Then, resins were measured by thermal analysis (Differential scanning colorimeter:SII DSC6200), Mw(Gel permeation chromatography: TOSOH Shodex System-21), composition ratio (NMR: JEOL AL-400), transmittance (UV: SHIMADZU UV-2500PC) to compared with reference sample (free-radical polymerization method).

2.3 Lithography Evaluation

The polymers were dissolved in propylene glycol monomethyl ether acetate and ethyl lactate along with a standardized amount of a photo acid generator and quencher. The photosensitive solution was spin-coated onto silicon wafer with organic bottom anti-reflective coating (BARC), soft baked for 60s at each temperature, exposed, post exposure bake(PEB) for 60s at each temperature, and developed using 2.38% aqueous tetramethyl ammonium hydroxide. Nikon scanner (NSR-S302A: NA=0.60) was used as exposure unit in this experiment.

2.4 Thermal Flow Procedure

To thermally flow, the post-development bake was applied to the resist pattern after the development.

3. Results and Discussions

3.1 Effect of Polymer Composition for Thermal Flow

It is considered that thermal flow performance is basically depending on the polymer's thermal property. This time, in order to split the polymer $T_g$, below 4 polymers are prepared by changing the monomer type and acrylate ratio (Table.1) The table.2 shows GPC, NMR, and transmittance of each polymer. With RAFT polymerization, the PDI are all controlled as below 1.5.

Table.1 Evaluation sample matrix for thermal flow property

<table>
<thead>
<tr>
<th>Resin</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer_1(40%)</td>
<td>EAdA</td>
<td>EAdA</td>
<td>EAdMA</td>
<td>EAdMA</td>
</tr>
<tr>
<td>Monomer_2(40%)</td>
<td>NBLA</td>
<td>GBLA</td>
<td>NBLA</td>
<td>GBLA</td>
</tr>
<tr>
<td>Monomer_3(20%)</td>
<td>HAdA</td>
<td>HAdA</td>
<td>HAdA</td>
<td>HAdA</td>
</tr>
<tr>
<td>Acryl ratio</td>
<td>100%</td>
<td>100%</td>
<td>60%</td>
<td>60%</td>
</tr>
</tbody>
</table>

![Chemical Structures]

Table.2 Analysis results of basic measurement for low dispersion polymer

<table>
<thead>
<tr>
<th>Resin</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal analysis ($T_d/T_g$)</td>
<td>196/144°C</td>
<td>190/102°C</td>
<td>179/145°C</td>
<td>184/127°C</td>
</tr>
<tr>
<td>GPC (Mw / Mw/Mn)</td>
<td>11000/1.31</td>
<td>10900/1.36</td>
<td>9200/1.38</td>
<td>10900/1.46</td>
</tr>
<tr>
<td>NMR (Monomer 1/2/3)</td>
<td>36.9/41.1/22.0</td>
<td>38.3/42.3/19.4</td>
<td>42.5/36.7/20.8</td>
<td>41.6/39.1/19.3</td>
</tr>
<tr>
<td>Absorbance (1/um @193nm)</td>
<td>0.29</td>
<td>0.3</td>
<td>0.32</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Figure.1 shows the thermal flow rate of dense contact hole with each polymer. This lithography test is based on thermal flow from 140nm with 170nm mask size(300nm Pitch). Because the each polymer has different $T_g$, the flow temperatures were different. However, in term of the flow rate control(nm/°C), the Polymer III and IV shows fairly stable flow rate. As the result, it is clear that the polymer, which has the protection group requiring high energy to detach, probably has more stable flow rate because the unexposed area has small flow.
3.2 Effect of polymer weight for thermal flow

Here, we have investigated the thermal flow effect on different molecule weight. In this experiment, we used Resin III for all the split. Also, as the reference, we also prepared same polymer of conventional radical type, which has larger disparity (Middle and III are same).

<table>
<thead>
<tr>
<th>Resin</th>
<th>Small</th>
<th>Middle</th>
<th>High</th>
<th>Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal analysis (Td/Tg)</td>
<td>194/137°C</td>
<td>179/145°C</td>
<td>194/141°C</td>
<td>190/129°C</td>
</tr>
<tr>
<td>GPC (Mw / Mw/Mn)</td>
<td>5600/1.32</td>
<td>9200/1.38</td>
<td>15000/1.41</td>
<td>11200/2.24</td>
</tr>
<tr>
<td>NMR (Monomer 1/2/3)</td>
<td>40.9/41.2/17.9</td>
<td>42.5/36.7/20.8</td>
<td>41.1/38.7/20.2</td>
<td>40.3/40.3/19.6</td>
</tr>
<tr>
<td>Absorbance (1/um @193nm)</td>
<td>0.32</td>
<td>0.32</td>
<td>0.29</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Figure 2 shows the thermal flow rate of dense hole. In comparison of PDI, larger molecule weight shows more stable thermal flow rate. Also, at the same molecule weight, wide PDI polymer, compared to narrow PDI polymer, shows worse thermal flow rate, and it seems that narrow PDI polymer has better flow control. We believe that at the same molecule weight, because the low PDI has less amount of small molecule weight area, the Tg tends to be higher and this is the reason why the thermal flow rate is more stabilized.

3.3 Effect of low PDI polymer for litho performance

In order to check the lithography performance of thermal flow, with Resin IV, we compared the performance between narrow and wide PDI. In this thermal flow, 140nm hole size can be gained from 160nm hole with 20nm shrink so that compared to the normal lithography, the DOF enhancement can be expected. Figure 3 shows the resolution performance and Figure 4 shows the DOF performance. As the result, narrow PDI has the larger common DOF and the profile circularity is better without losing the original resolution.
Fig. 3  Comparison of resolution performance of resists with each PDI resin

Fig. 4  Comparison of DOF performance of resists with each PDI resin

Fig. 5  Comparison of DOF performance of resists with each PDI resin

4. Conclusions
We can gain wide DOF margin on contact hole pattern with low PDI polymer in thermal flow process. We believe this is very good advantage for preparation of thermal flow process in production level. In terms of thermal flow process itself, it is very important that this low PDI gives good control of flow rate in high temperature.

References