Mechanism Investigation of Filtration on Metal and Gel Removal from DSAL Resist

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Reduction of impurities such as gels and metals is one of the critical requirements in chemistries used in directed self assembly lithography (DSAL). In this study, we focused on elucidating the forms of the gels and metals in block copolymer (BCP) solution to effectively reduce these impurities. As a result, particles or gels, and ions are suggested as forms of metals. To reduce these multiple forms of metals, multistep filtrations such as repetitive filtration of single filter material and combination of different type of filters are conducted. As a result, more than 99.99% of Li and more than 99.9% of Al are reduced with a combination of Nylon 6,6 10 nm filtration and ion exchange filtration. The order of the filtration steps does not impact the removal efficiency. The results should contribute realizing DSAL in semiconductor device fabrication.

Keyword: filtration, ion exchange filter, Nylon 6,6, directed self assembly lithography, block copolymer

1. Introduction

Gel defect reduction is one of the critical requirements in block copolymer (BCP) layer of directed self assembly lithography (DSAL)[1]. In conventional chemically amplified resists (CAR), low solubility fragments such as large molecular weight polymer molecules and segregation of low solubility functional groups are the potential sources of gel defects. In DSAL, larger molecular weight of the BCP than that of CAR polymer might predominantly contribute gel defect excursion. We have evaluated filterability[2] and gel removal performance[3] on polystyrene-block-polymethylmethacrylate (PS-b-PMMA) based BCP solution and found that gels in the BCP solution can be significantly reduced after advanced lithography grade filtration without change in polymer concentration and molecular weight distribution both of which are critical for DSA performance. Further, material of the filter membrane is found to be critical for effective gel removal besides dimensional pore size which is indicated as a filter rating.

In conventional BCP polymerization, metal catalysts are used to conduct living polymerization. To meet the requirement on low metal concentration in advanced electronic materials, we have studied to reduce these metals using ion exchange filtration and microfiltration. As a result, the metals are removed not only with ion exchange filter but also with microfiltration membranes[3].

In the current work, the mechanism of metal removal with microfiltration is studied by analyzing contact time dependence of metal removal with various filter materials to differentiate whether the removal is a result of adsorption or sieving. Multistep filtration
is conducted for further metal reduction. Additionally, elucidation of the metal form in the BCP solution is explored.

2. Experimental

2.1. Test fluid

Polystyrene-block-polymethylmethacrylate (PS-b-PMMA), $M_w=35000$-b-$37000$ diblock copolymer, which corresponds to $20$ nm half pitch after lamellae type self assembly[4], is dissolved in electronics grade propylene glycol monomethyl ether acetate (PGMEA) at a concentration of $1.5\%$, then pre-filtered using $0.2\ \mu m$ rated polytetrafluoroethylene (PTFE) membrane filter. This BCP solution is used as an influent.

2.2 Test filters

Pall $10$ nm rated asymmetric Nylon $6,6$ membrane, Pall $2$ nm rated high density polyethylene (HDPE) membrane and Pall ion exchange filter membrane are used in $47$ mm diameter disk.

2.3 Track etch membrane

It4ip hydrophilic polyimide track etch membrane (pore diameter $= 30$ nm, thickness $= 12\ \mu m$ and pore density $= 6\times10^9/cm^2$) is used to evaluate the gel amount in the test filter effluents. Prior to the testing, flow rate of the track etch membranes are measured with passing PGMEA to select consistent flow membranes.

2.4. Contact time dependence test

Contact time between the test fluid and the test filter membrane is calculated using equation (1).

$$\text{Contact time} = \frac{\text{Filter area} \times \text{Thickness}}{\text{Flow rate}} \quad (1)$$

Efficiency of adsorption is dependent on contact time between the filtration fluid and the filter membrane. Contact time dependence on metal removal efficiency is evaluated to understand the removal mechanism in filtration using various kind of membranes.

Test fluid is passed through each test filter using a static pressure filtration test stand shown in Figure 1. Flow rate, which is directly correlated to the contact time is controlled with adjusting inlet pressure or the needle valve at downstream of the filter.

![Figure 1. Pressurized filtration stand.](image)

Contact times tested for each membrane are shown in Table 1.

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>Contact time</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE 2 nm</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.58</td>
</tr>
<tr>
<td>HDPE 2 nm</td>
<td>26</td>
</tr>
<tr>
<td>HDPE 2 nm</td>
<td>14</td>
</tr>
<tr>
<td>HDPE 2 nm</td>
<td>7.3</td>
</tr>
<tr>
<td>HDPE 2 nm</td>
<td>3.5</td>
</tr>
<tr>
<td>Nylon 6,6 10 nm</td>
<td>25</td>
</tr>
<tr>
<td>Nylon 6,6 10 nm</td>
<td>10</td>
</tr>
<tr>
<td>Ion exchange filter</td>
<td>4.4</td>
</tr>
</tbody>
</table>

2.5. Multistep filtration

Multistep filtration is tested besides contact time dependence. Figure 2 shows tested filtration steps. The test stand shown in Figure 1 is used for each step, a small portion of the effluent is sampled for metal analysis using inductive coupled plasma mass spectroscopy (ICP-MS, Agilent 7700s) and the remaining effluent is used for the subsequent steps of the filtration.
2.6. Gel removal in ion exchange filter

In a previous study[3], it was found that non-polar HDPE 2 nm membrane which is regarded not having any adsorption capability of metals, unexpectedly reduced metals for some extent. Based on this, it is assumed that some portion of metal forms gels or particles so that the metals are sieved by HDPE 2 nm membrane. To confirm this from a different perspective, gel removal capability of the adsorptive ion exchange filter is evaluated.

Using filtration test stand shown in Figure 1, an influent and an effluent BCP solution of the ion exchange filter are passed through track etch membrane at 180 kPa of the inlet pressure. Flow decay of the track etch membranes indicates relative gel and particle amount contained in the fluid samples tested.

Gels or particles that may clog the track etch membrane are then observed using scanning electron microscopy (SEM, Hitachi S-4700). To avoid unwanted precipitation of the BCP in drying, the track etch membranes are flushed with 20 ml of PGMEA after passing BCP solution.

3. Results and Discussion

3.1. Metal concentration in BCP solution

Figure 3 shows metal concentration in 1.5% PS-b-PMMA/PGMEA solution. As a result, concentrations of Al and Li are substantially high. These metals are assumed to be derived from polymer synthesis[5].

3.2. Contact time dependence

Based on the results that Al and Li are the dominant metal content in the BCP solution, these elements are focused in this section. Figure 4a-c shows contact time dependences of Al and Li reduction in various membrane filtrations. As shown in Figure 4a for HDPE 2 nm membrane filtration, Al and Li are removed at a certain efficiency, but with no contact time dependence, indicating that the removal is not by adsorption.

As shown in Figure 4b, Nylon 6,6 10 nm membrane best reduced both Al and Li among the three membranes. Filter rating such as 10 nm and 2 nm is determined using retentive particle size in gold nanoparticle challenge test which represents sieving performance. And the sieving performance of Nylon 6,6 10 nm membrane is lower than that of HDPE 2 nm. The higher Al and Li removal efficiency observed here should be increased by other mechanism. Besides sieving, adsorption is considered to increase the efficiency. And slightly observed contact time dependence on the removal efficiency also indicates the contribution of adsorption.

Figure 4c is the result in ion exchange membrane filtration, clearly shows the removal efficiency is contact time dependent. An adsorption kinetics equation is used to fit the results. The high coefficient of determinations ($R^2 > 0.99999$) for both metals indicate that these metals are removed with adsorption. Adsorption orders of $\sim 1$ indicate that these metals are removed in pseudo-first order, which is expected in a condition in “adsorbents (adsorption site in ion exchange filter)>>adsorbates (metals)”.

Figure 2. Test condition in multistep filtration.

Figure 3. Metal concentration in 1.5% PS-b-PMMA/PGMEA solution.
3.3. Multistep filtration

Results in the previous section also indicate that single step filtration for all kind of the tested membrane has a plateau at a certain contact time. Even in Nylon 6,6 10 nm, the maximum removal efficiency at the longest contact time (=26 sec.) is 0.98 (=98%) for both Al and Li and single digit ppb of metals are detected in the effluents. To further reduce these metals, an alternative method such as multistep filtration is tested.

Figure 5a shows results of repetitive filtration using Nylon 6,6 10 nm membrane. More than 98% reduction is observed in the first step, but further reduction in the second and third steps are not significant. This indicates that contact time extension and repetitive filtration are intrinsically the same in Nylon 6,6 10 nm filtration on the BCP solution for metal removal.

Figure 5b shows the result of Nylon 6,6 10 nm followed by Ion exchange filter (IEX). This double step filtration is significantly effective and both metals are reduced to less than 1 ppb. Figure 5c shows the result when the membrane order of the Nylon 6,6 10 nm-IEX double step filtration is switched. The metal concentrations also significantly reduced in this condition. The results show that membrane order of these double step filtrations does not impact the effluent metal concentration. Metal holding capacity is another concern to determine the membrane order, because approximately 100 times larger amount of metals are loaded on the first step membrane, and should be a subject of future study.

A plateau in the metal removal efficiency is found in the single step contact time dependence test. In contrast, the multistep filtration with different kind of membrane further reduced metal concentration. Based on this, irreducible metal forms with either type of the membrane exist in the PS-b-PMMA/PGMEA solution.

Further, existence of ions is suggested as irreducible metal forms of Nylon 6,6 10 nm membrane because such metals are reduced with following ion exchange filter.

Metal concentration for 13 metal elements in multistep filtration is shown in Table 2. Metal removal efficiency in Nylon 6,6 10 nm and ion exchange filter combination for Li is calculated as greater than 99.99% and for Al greater than 99.9% in both membrane orders. Metals other than Al and Li are also reduced to low level after any of the multistep filtrations.
3.4 Gel removal in ion exchange filter

Figure 6 shows the clogging of the track etch membrane which indicates the cleanliness of the test fluids. As a result, flow decay of the track etch membrane used for the ion exchange filter effluent is significantly lower than that of influent, this indicates that gels or particles are removed with ion exchange filter.

Sieving capability of the ion exchange filter is expected to be lower than 0.2 μm rated PTFE membrane which is used to prepare the PS-b-PMMA/PGMEA solution. Therefore, no large gels or particles that can be sieved by ion exchange filter is expected to be in the influent. Based on this, the gels or particles removal with ion exchange filter should be done by adsorption, including ion exchange reaction. And the fact that ion exchange filter exhibits high affinity to the metals, existence of gels or particles that contains metals is assumed.

Figure 7 shows SEM image on the track etch membrane filtration for influent and effluent of ion exchange filter. 1.5% PS-b-PMMA/PGMEA solution. Flow rate decay indicates gel or particle content in the test fluid.

### Table 2: Metal concentration in 1.5% PS-b-PMMA/PGMEA solution after multistep filtration. Unit: ppb. QL=quantification limit.

<table>
<thead>
<tr>
<th></th>
<th>QL</th>
<th>Influent</th>
<th>N66 3 times</th>
<th>N66-IEX</th>
<th>IEX-N66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.001</td>
<td>148</td>
<td>0.085</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>Na</td>
<td>0.007</td>
<td>6.6</td>
<td>0.53</td>
<td>0.015</td>
<td>0.030</td>
</tr>
<tr>
<td>Mg</td>
<td>0.008</td>
<td>13</td>
<td>0.085</td>
<td>0.094</td>
<td>0.074</td>
</tr>
<tr>
<td>Al</td>
<td>0.2</td>
<td>294</td>
<td>2.3</td>
<td>&lt;QL</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>K</td>
<td>0.03</td>
<td>1.4</td>
<td>0.34</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca</td>
<td>0.08</td>
<td>1.6</td>
<td>0.20</td>
<td>0.09</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>Cr</td>
<td>0.04</td>
<td>0.12</td>
<td>&lt;QL</td>
<td>&lt;QL</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>Mn</td>
<td>0.01</td>
<td>0.22</td>
<td>0.04</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1</td>
<td>6.4</td>
<td>0.4</td>
<td>*</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.14</td>
<td>0.14</td>
<td>0.37</td>
<td>0.31</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03</td>
<td>0.21</td>
<td>&lt;QL</td>
<td>&lt;QL</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>Zn</td>
<td>0.1</td>
<td>1.4</td>
<td>0.4</td>
<td>0.27</td>
<td>&lt;QL</td>
</tr>
<tr>
<td>Pb</td>
<td>0.04</td>
<td>0.03</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*: Experimental error
etch membrane used to pass influent and effluent of ion exchange filter. Larger amount of gels or particles are found on the membrane used for the influent. These images suggest that ion exchange filter does not only remove ions but also substances that exhibit certain size.

![SEM images on the track etch membrane which is used to pass BCP solutions. a: influent, b: effluent of exchange filter. Filtration volume through the track etch membrane is 50 g. 1.5% PS-b-PMMA/PGMEA solution. Pore diameter of the track etch membrane is 30 nm.](image)

**Figure 7.** SEM images on the track etch membrane which is used to pass BCP solutions. a: influent, b: effluent of exchange filter. Filtration volume through the track etch membrane is 50 g. 1.5% PS-b-PMMA/PGMEA solution. Pore diameter of the track etch membrane is 30 nm.

**4. Conclusion**

Contact time dependence test in PS-b-PMMA solution revealed that metal removal mechanism with various membranes as follows: HDPE 2 nm filtration; pure sieving, Nylon 6,6 10 nm filtration; sieving and adsorption, ion exchange filtration; pure adsorption.

Multistep filtration results suggested that Nylon 6,6 10 nm membrane and ion exchange membrane complement each other for some irreducible metal forms with either type of the membrane. And this membrane combination achieved Li reduction greater than 99.99% and Al reduction greater than 99.9%.

Particulate or gel like form are evidenced as the form of metals in the BCP solution, based on gel reduction by non-sieving ion exchange filter, supplementarily to metal reduction by sieving with HDPE 2 nm filtration.

It is notable that establishment of the efficient removal process of metals, which is probably added in polymer synthesis, should contribute realizing DSAL in semiconductor device fabrication.

**References**


