Filtration on block copolymer solution used in directed self assembly lithography

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ABSTRACT

In this paper, we presented the filtration effects on block copolymers (BCP) that are commonly used in directed self-assembly lithographic (DSAL) imaging schemes. Specifically we focused on filtration effects on micro-contaminants such as metal ions and metal induced gels.

Gel removal efficiency studies carried out with HDPE, Nylon and PTFE filters pointed out that Nylon 6,6 membrane is the most effective in removing gels in block copolymer (BCP) solutions.

Metal removal efficiency studies were conducted using multistep filtrations such as repetitive filtration of single membrane material and combination of different type of membranes. Results showed that a combination of Nylon-6,6 and ion-exchange filters is highly effective in reducing metals such as Li, Mg and Al to > 99.99% efficiency. The mechanism of metal removal efficiency is discussed in detail.

Keywords: Filtration, Ion exchange filter, Nylon 6,6, Directed self assembly lithography, Block copolymer

1. INTRODUCTION

Directed self assembly lithography (DSAL) is studied actively as a candidate for next generation lithography. Since materials employed in DSAL are considerably different from conventional chemically amplified resists (CAR), an independent study on the filtration should be conducted. We have investigated the block copolymer (BCP) filtration in terms of its impact on the polymer characteristics and gel/metal reduction [1-3]. As shown in Table 1, molecular weight of the block copolymer used in DSAL resist is substantially larger than conventional CAR. It can be anticipated that aggregated gels of low solubility molecules should be produced easily with the high molecular weight polymer due to its limited solubility. In fact, gel particles are reported as the predominant defects in BCP layer in a DSAL processes [4]. In photoresists, removal efficiency for the gels is known to highly depend on the filtration materials[5]. We have examined this dependency on the BCP solution and will report in this paper.

Table 1. Resist polymer properties[6]

Lithography	DSAL	ArF, ArFi
Polymer	Block copolymer	Random copolymer
Poly dispersity index (PDI)	~1.1	~2
Molecular weight (Mw)	~100000	6700-7100

Metal catalysts are used in living polymerization, which is a common BCP production step. 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[2]. In the current work, the mechanism of metal removal with filtration is studied by analyzing contact time dependence of metal removal with various membrane materials to differentiate whether the removal is a result of adsorption or sieving. Multistep filtration is conducted for further metal reduction.

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2. EXPERIMENTAL

2.1 Gel reduction

Using a constant pressure filtration test-stand shown in Figure1, left, the effluents of the 1.5% PS-b-PMMA (Mw=35000-b-37000) BCP in propylene glycol monomethyl ether acetate (PGMEA) were collected. The for "test filters" used are 2 nm high density polyethylene (HDPE) filter, 10 nm nylon 6,6 filter and 20 nm poly tetra fluoroethylene (PTFE) filter. To evaluate the cleanliness of the obtained effluents, the collected effluents were filtered using a "standard filter", which is a track etch membrane with 30 nm pores as shown in Figure 1, right. The clogging of the standard filter should depend on the amount of gels in the test filter effluents. A resistance coefficient in the Darcy's law is calculated as a degree of clogging for the standard filter. Equation (1) is the Darcy's law, which is a fundamental relationship among each component in filtration.

$$\mathrm{dP}=\frac{k\mu Q}{A} \qquad (1)$$

Where: dP=differential pressure of the filter(Pa), k=flow resistance coefficient(m^{-1}), μ=fluid viscosity(Pa·sec), Q=flow rate(m^3/sec) and A=filter area(m^2)

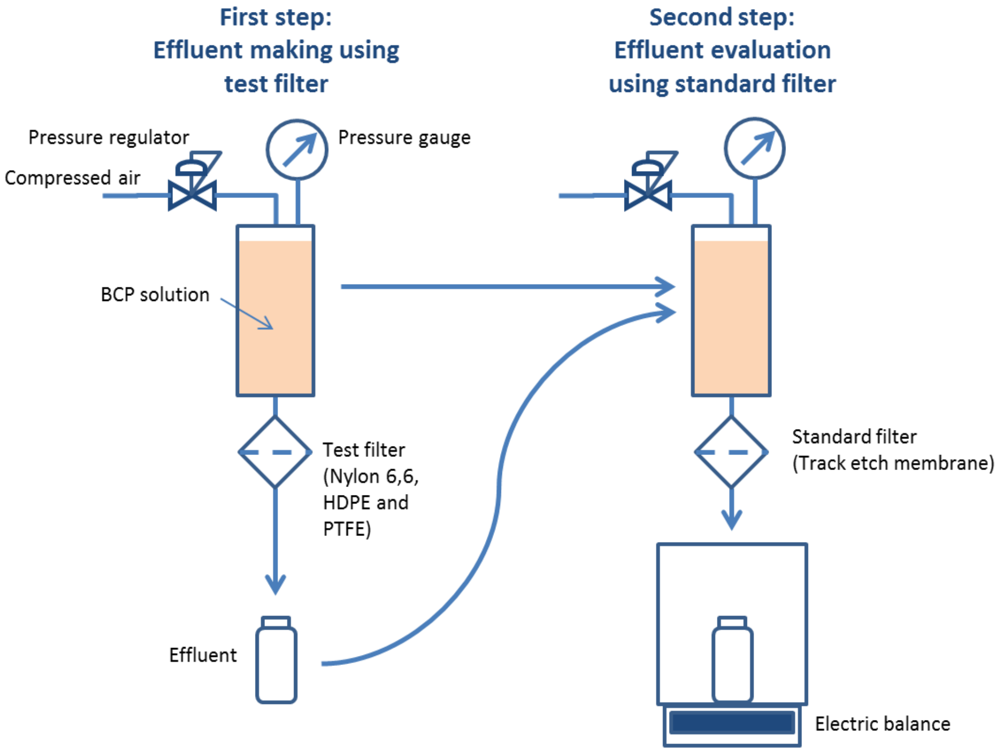

Figure 1. Schematic illustration of the gel removal performance evaluation using track etch membrane.

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2.2 Metal reduction

2.2.1 Contact time dependence

Contact time between the test fluid and the test filter membrane is calculated using equation (2).

$$\text{Contact time} = \frac{\text{Filter area} \times \text{Thickness}}{\text{Flow rate}} \qquad (2)$$

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, left. 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. Metal analysis using inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7700s) is conducted on the influent and effluents.

2.2.2 Multistep filtration

Multistep filtration is tested besides contact time dependence. Figure 2 shows tested filtration steps. The test stand shown in Figure 1, left is used for each step, a small portion of the effluent is sampled for metal analysis using ICP-MS and the remaining effluent is used for the subsequent steps of the filtration.

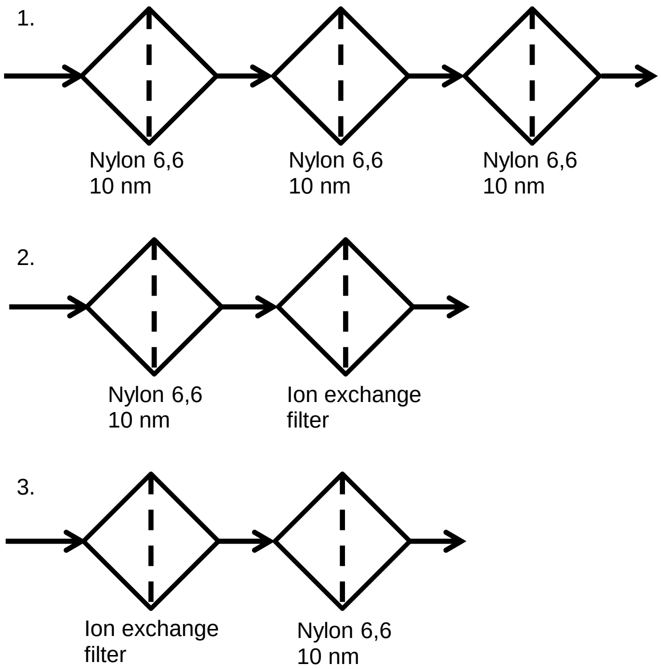

Figure 2. Test conditions in multistep filtration.

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3. RESULTS AND DISCUSSIONS

3.1 Gel reduction in BCP solution

A flow resistance coefficient (k) shown in Figure 3 is the clogging of the track etch membrane which we utilized to quantitatively indicate the cleanliness of the test filter effluents (the lower the cleaner). As a result, k for the 10 nm nylon 6,6 filter was the lowest, indicates this filter best reduced gels in the 1.5% PS-b-PMMA/PGMEA solution.

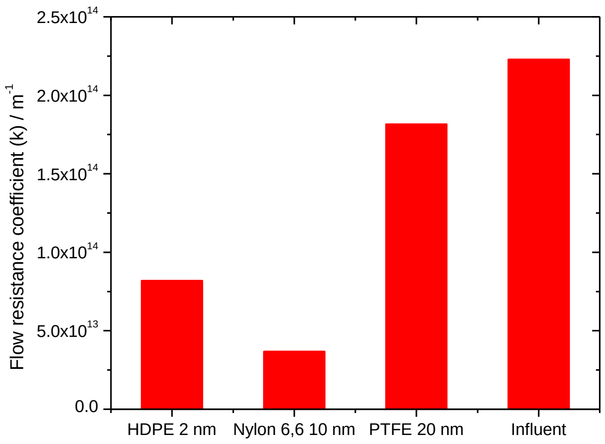

Figure 3. Flow resistance coefficient (k) of 30 nm track etch membrane at 40 g throughput in filtration for the test filter effluents. x axis indicates the test filters. Test fluid is 1.5% PS-b-PMMA/PGMEA solution.

The k is further analyzed for the test filter properties such as thickness, rating, contact time during filtration and critical wetting surface tension (CWST) as shown in Figure 4. As a result, k correlated with contact time and CWST, both of which indicates chemical interaction like adsorption. k did not well correlated with thickness and ratings. This probably indicates these physical properties less contribute the gel reduction in the BCP solution.

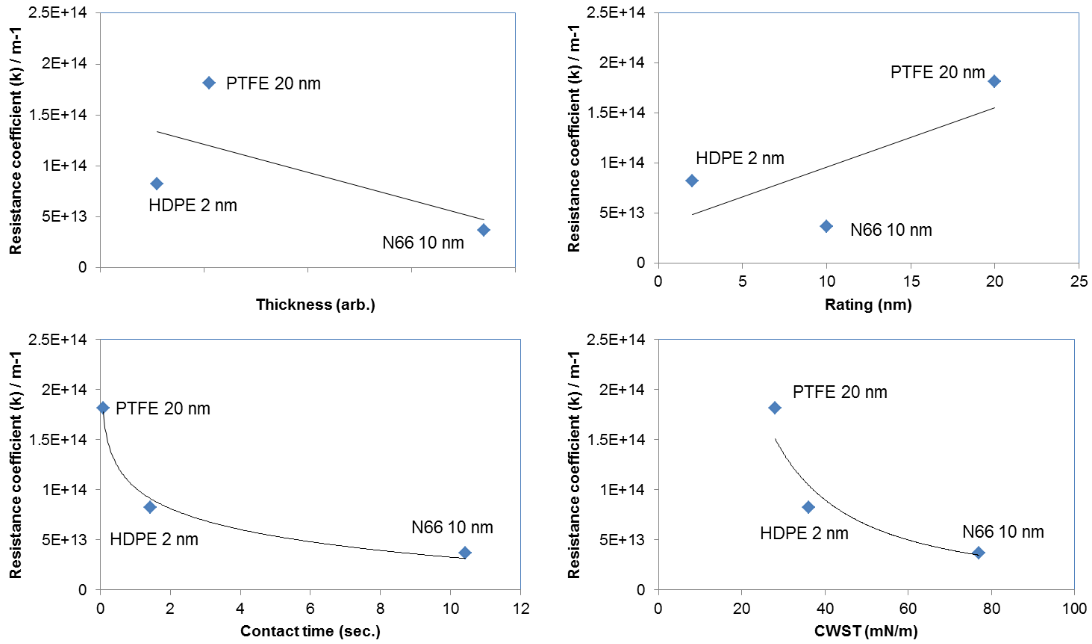

Figure 4. Filter properties vs. flow resistance coefficient (k) in effluent filtration using track etch membrane.

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3.2 Metal reduction in BCP solution

3.2.1 Contact time dependence

Al, Li and Mg are the top three metal contents in the BCP solution and these elements are focused in this section. Figure 5. shows contact time dependences of Al, Li and Mg concentration in the effluents of various membrane filtrations.

For 2 nm HDPE membrane filtration as shown in Figure 5, left, metals are removed at a certain efficiency, but with no contact time dependence. This indicates that the removal is not by adsorption.

As shown in Figure 5, center, 10 nm nylon 6,6 filter best reduced Al, Li and Mg among the three filter membranes. Contact time dependence is observed in Al concentration, indicating that the adsorption is the dominant mechanism. Contact time dependence is not observed in Li and Mg, but lower metal concentration than the effluents of finer rated HDPE membrane indicates that the reduction is not made by sieving. Adsorption probably played a role in Li and Mg reduction.

Figure 5, right is the result in ion exchange membrane filtration, clearly shows the metal reduction is contact time dependent.

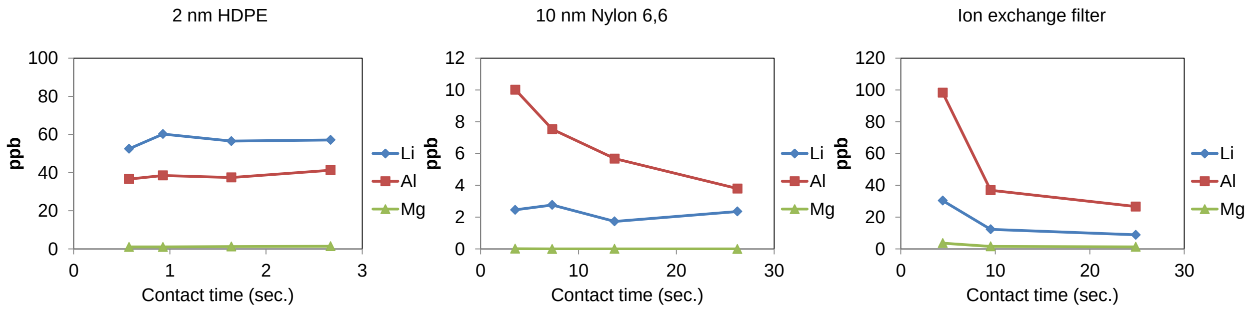

Figure 5. Contact time dependence of Li, Al and Mg in effluents of various filtration membrane materials. Influent metal concentration: Li=148 ppb, Al=294 ppb and Mg=13 ppb. 1.5% PS-b-PMMA in PGMEA.

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3.2.2 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 10 nm nylon 6,6, single digit ppb of Li and Al are detected in the effluents at the longest contact time (=26 sec.). To further reduce these metals, an alternative method such as multistep filtration is tested.

Left row of the Figure 6 shows results of three times repetitive filtration using 10 nm nylon 6,6 membrane. Significant reduction is observed in the first step, but not in the second and third steps. This indicates that contact time extension tested in the previous section and repetitive filtration are essentially the same in 10 nm nylon 6,6 filtration on the BCP solution for metal removal.

Center row of Figure 6 shows the result of 10 nm nylon 6,6 followed by Ion exchange filter (IEX). This double step filtration is significantly effective and most of all metals are reduced to less than 1 ppb. Right row of Figure 6 shows the result when the membrane order of the 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 final 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, some metal which is irreducible with either type of the membrane possibly exists in the PS-b-PMMA/PGMEA solution. Further, existence of ions is suggested as metal irreducible with 10 nm nylon 6,6 membrane because such metals are reduced with following ion exchange filter.

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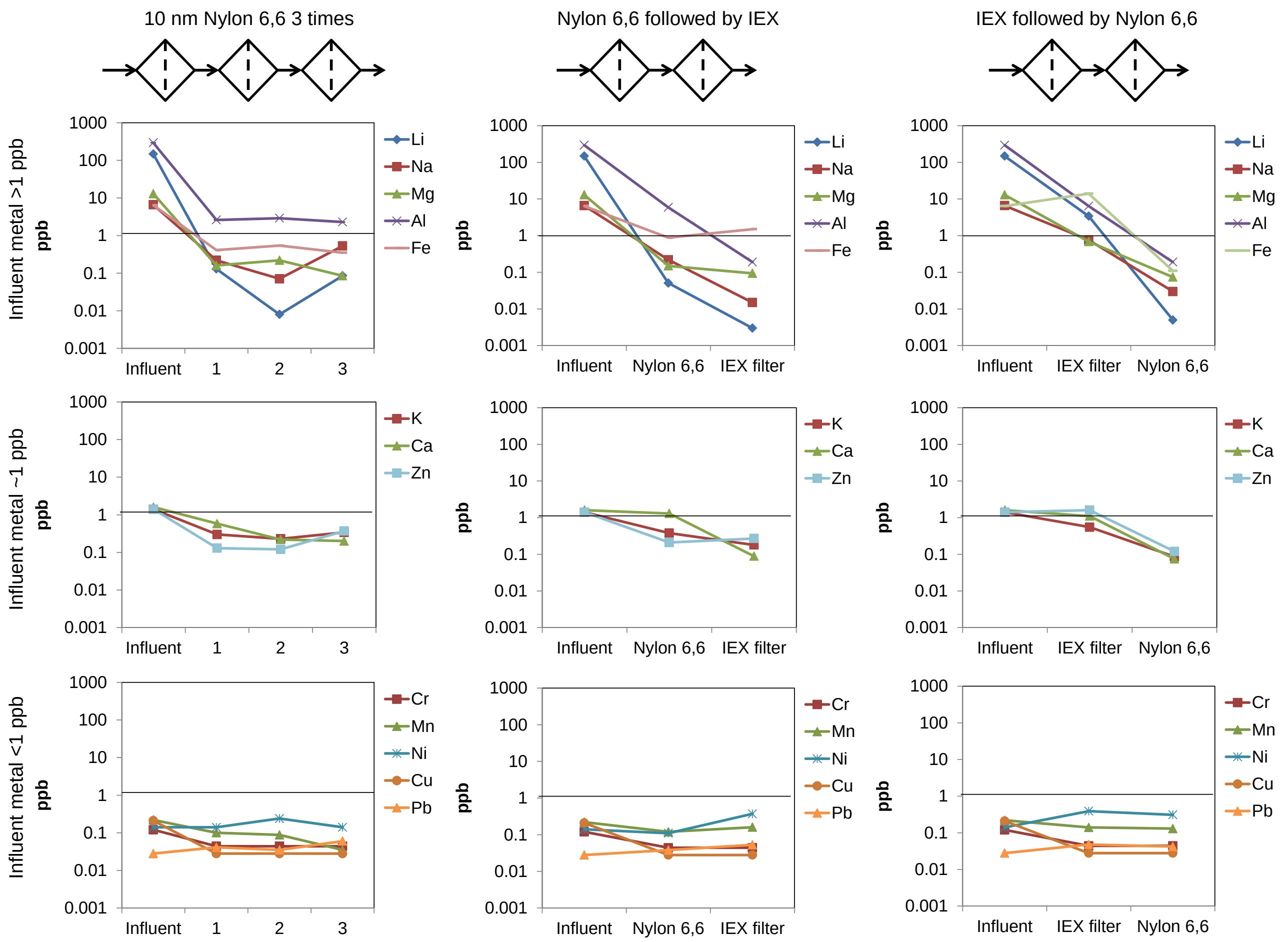

Figure 6. Multistep filtration results in 1.5% PS-b-PMMA/PGMEA solution. Contact time for each step of 10 nm nylon 6,6 filtration is 7.3 sec. and for IEX filter is 25 sec. Concentrations below quantification limit (QL) of ICP-MS analysis are plotted at the QL values.

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4. CONCLUSION

Gel reduction test using track etch membrane is found to be capable of differentiating the performance of the lithography process filters in DSAL BCP solution. As a result, 10 nm nylon 6,6 membrane best reduced gels. And adsorption was found to be effective in reducing the gels in BCP solution, with the flow resistance coefficient analysis.

Contact time dependence test in PS-b-PMMA solution revealed that metal removal mechanism with various membranes as follows:

2 nm HDPE filtration; sieving

10 nm nylon 6,6 filtration; sieving and adsorption

Ion exchange filtration; adsorption.

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

The establishment of the efficient removal process of metals should contribute realizing DSAL in semiconductor device fabrication.

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