Filtration condition study for enhanced microbridge reduction

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ABSTRACT

Filtration products utilizing Nylon 6,6 membrane technology have demonstrated effectiveness in reducing microbridge defects in DUV photoresist patterning. The effects of fluid flow characteristics on defect reduction using a point-of-use Nylon 6,6 filtration product are explored. Lower filtration pressure and longer contact time were found to enhance the removal of gel-like microbridge defect precursors during point-of-use filtration of photoresist polymer solution. A kinetic study of high-pressure filtration, where a strong dependency of gel removal on contact time is observed, revealed the gel-like precursors are adsorbed to a greater extent at sites of polar Nylon 6,6 throughout the membrane depth. A study of gel capturing position by ICP-MS for low-pressure filtration, where gel removal is independent of contact time, revealed the gels are captured at the inlet portion of the filter, due to smaller transportation force, as compared to deeper into the filter media depth.

These findings will be very useful both in optimizing filter operating procedures and in the development of next-generation filtration products, ultimately contributing toward reduced defectivity and increased yield within next-generation lithography processes.

Keywords: Filtration, Photoresist, Nylon 6,6, Adsorption kinetics, Asymmetric

1. INTRODUCTION

As lithographic pattern CDs continue to shrink, so does the tolerance for the size of photo resist defects, such as agglomerated microbridge precursors. Greater demands will certainly be placed on the cleanliness of next-generation lithography process fluids. Filtration products utilizing Nylon 6,6 membrane technology have demonstrated effectiveness in reducing microbridge defects in DUV photoresist patterning.[1-4] Recent work revealed that adsorption of gel-like precursors onto Nylon 6,6 membrane media was the primary mechanism driving microbridge defect reduction.[5] In the present work, the effects of fluid flow characteristics on defect reduction using a point-of-use Nylon 6,6 filtration product, Pall Asymmetric P-Nylon Filter Assembly, are explored. Flow rate, filtration pressure, and membrane volume (Thickness × Area) were varied and filter membranes were analyzed for effects on adsorption performance from the point of view of contact time—a parameter commonly used in catalytic chemistry and other time-dependent processes.

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2. EXPERIMENTAL

2.1 Gel removal test

Within the photoresist solution, microbridge precursors are thought to exist as a gel-like substance. Formation of microbridge precursors can be encouraged by spiking an ArF photoresist polymer solution with metal ions, which act as quasi-nucleation sites around which the nearly insoluble resist polymer components may aggregate.[5]

A concentration of 10 ppb of Mg ion was spiked into ArF photoresist polymer solution and aged for 48 hours to enhance gel aggregation. Filtration testing was conducted using the spiked photoresist solution, at constant pressure, with a 47-mm disk of Pall Asymmetric P-Nylon Filter membrane for advanced photoresist technology. The asymmetric Nylon 6,6 media was oriented with the fine pores on the downstream side. Filter inlet pressure, flow rate, and filter thickness (number of media layers) were varied to establish test parameters and contact time, following equation (1) below, and as indicated in Table 1. The filter inlet pressure was varied from 0.01 MPa to 0.2 MPa with atmospheric outlet pressure. Flow rate was varied from 0.80 g/min to 8.5g/min. For thickness, one to three layers of filter membrane were stacked. To confirm that the bonding of the filter membrane layers had no effect on flow resistance, the linearity of flow rate against reciprocal of stacking number was confirmed. Contact time was normalized against Test No. PL-1 (Table 1) and expressed as relative values.

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

Gel removal efficiency was calculated by Mg concentration in filtrate measured by inductively coupled plasma-mass spectrometry (ICP-MS), since gel-like substance includes Mg (via nucleation on the metal ion).

Table 1. Experimental conditions for gel removal test

Test No.	Pressure group	Filter inlet pressure /MPa	Contact time /a.u.	Flow rate /g min^{-1}	Filter thickness /number of layer
PL-1	Low	0.06	1	8.5	3
PL-2		0.06	2	1.1	1
PL-3		0.01	9	1.0	3
PL-4		0.02	11	0.8	3
PH-1	High	0.20	1	2.5	1
PH-2		0.20	3	1.7	2
PH-3		0.20	7	1.2	3
PH-4		0.20	8	1.0	3

Contact time is relative value normalized against Test No. PL-1.
a.u.: arbitrary unit

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2.2 Gel capture within the filter depth

The three-layer filter stack, after being tested at the conditions noted in Table 2, was separated into individual layers, which were then analyzed by ICP-MS after ashing and subsequent dissolution into nitric acid. The amount of captured gels in each layer was measured as concentration of Mg.

Table 2. Test condition for gel capturing position analysis.

Test No.	Pressure group	Filter inlet pressure /MPa	Contact time /a.u.	Flow rate /g min^{-1}	Filter thickness /number of layer
D-PL-1	Low	0.02	5	1.7	3
D-PL-2		0.02	88	0.1	3

3. RESULTS AND DISCUSSIONS

3.1 Gel removal test

Evaluation of the results on gel removal efficiency, expressed as Mg removal efficiency, and the effect of contact time, are shown in Figure 1. At a high-pressure condition (0.2 MPa), Mg removal efficiency shows a strong positive correlation with contact time. This is a typical phenomenon observed in chemical reactions, including adsorption reactions, which will be mentioned in the next section. This result is supported by a previous observation that Nylon 6,6, compared to HDPE, is more effective in microbridge reduction at point-of-use filtration, mainly due to adsorption that is driven by electrostatic attraction to polar peptide bonds on Nylon 6,6. At low pressure, (<0.06 MPa), Mg removal efficiency is independent of contact time. Moreover, removal efficiency is consistently greater than at high pressure.

A pressure effect model[6] reported for methyl cellulose filtration using glass fiber filter in a range of 0.02 – 0.15 MPa with SEM observation seems applicable to these observed results. The model explains that increased pressure drives gels to permeate the filter media depth. Thus, at a high-pressure condition, gels are adsorbed to a greater extent at sites throughout the membrane depth. The gel adsorption is assumed to occur in proportion to the difference between affinity to adsorption sites and detaching force caused by bulk flow. This mechanism is similar to common chemical reaction models. Results given in Figure 1 show that Nylon 6,6 media effectively captures gels using adsorption sites that are positioned well within the filtration medium depth, even though the gel may not be captured at the inlet filter medium surface. Conversely, at lower pressure, gels interact primarily with the inlet filter media surface. Figure 2 illustrates an interpretation of the results according to the pressure effect model. At a low-pressure condition, there is less upstream force to drive gels into the filter media depth. Thus, gels adsorb primarily onto the filter media surface, leading to a weaker dependence of removal efficiency on contact time. Furthermore, less penetration of gels through the membrane thickness leads to greater removal efficiency.

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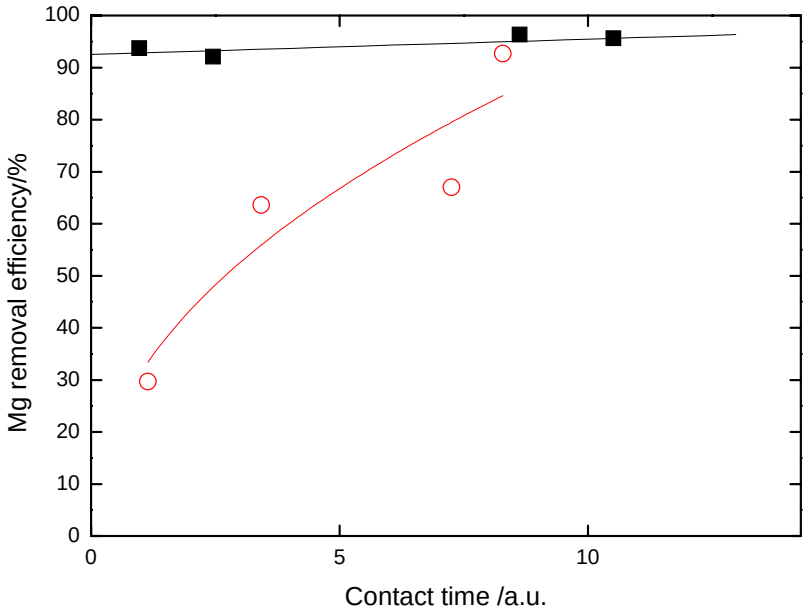
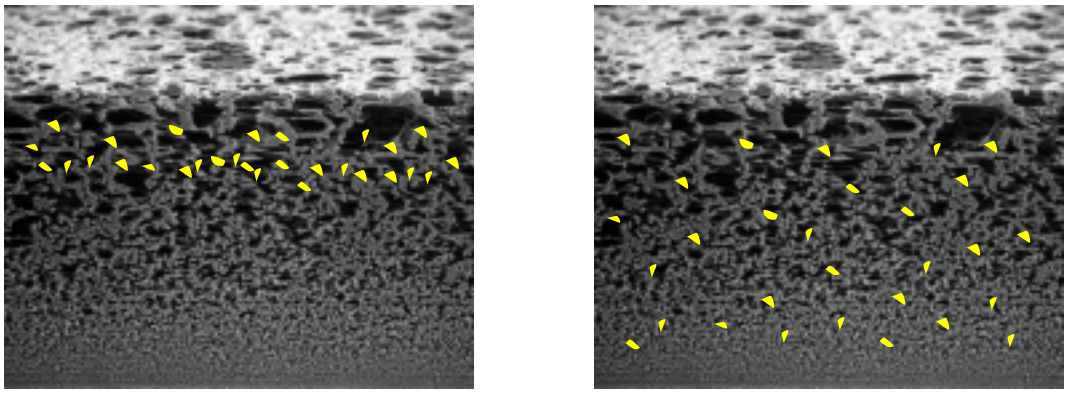


Figure 1. Mg removal efficiency against contact time at different filtration pressures with Mg-ion-spiked ArF resist polymer solution: ■ Filtration pressure <0.05MPa; ○ Filtration pressure 0.2MPa



At low pressure: Gels interact primarily at the surface.

At high pressure: Gels are adsorbed to a greater extent at sites throughout the membrane depth

Figure 2. Schematic interpretation of pressure effect model for gel filtration [6], as applied to results given in Figure 1, Yellow mark indicates gels captured by the filter media.

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3.2 Gel capturing position in filter depth direction

It is easily understood, in the high-pressure filtration mode, that gels containing Mg are captured throughout the media. This is evident as Mg removal efficiency was low when contact time was small, as shown in Figure 1. In order to verify the explanation for low-pressure filtration, the depth of gel capture was studied by measuring Mg content within individual filter media layers, as described in Table 2.

Mg concentrations in the low-pressure-tested filters are shown in Figure 3. The filters tested at low pressure show the overwhelming majority of Mg content being captured in the first layer. Even with a contact time difference of 88:5, results showed a very small difference in captured Mg content in the first layer, where in both cases capture percentage is 95%. This supports the explanation mentioned in the previous section that, within the tested range, pressure changes the dominant process between gel transportation and gel adsorption. In the low-pressure mode, the detaching force of gels from the adsorption sites by bulk flow is so small that most gels are adsorbed around the inlet portion of the Nylon 6,6 media.

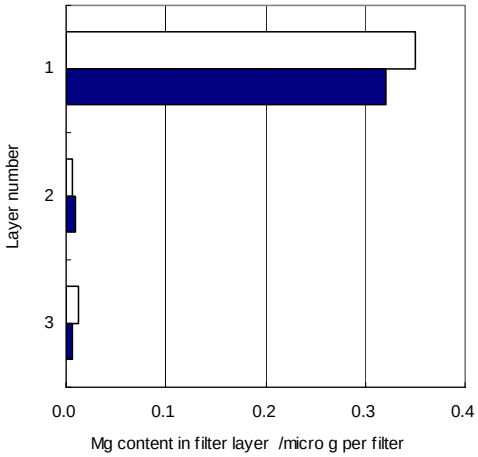

Figure 3. Mg content in layer of filter tested at low pressure corresponding to D-PL-1 and D-PL-2 in Table 2: □ D-PL-1; ■ D-PL-2

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3.3 Apparent adsorption kinetics

In order to verify that adsorption of gel-like precursors is dominant in filtration with Nylon 6,6, the kinetics of the adsorption was studied. Assuming a differential adsorption zone model, that is, assuming no distribution of adsorption rate in the whole membrane media zone, whose height is only a few hundred micrometers, the following equation (2) was applied to chemisorption in the liquid phase. The interfacial gradient of Mg concentration between adsorption sites on the Nylon 6,6 media and bulk fluid was not considered. Adsorption rate constant (k) and adsorbing reaction order (n) were fitted using the gel removal test data in Table 1.

$$r = kC^n \tag{2}$$

r : adsorption rate $[mol/s \cdot m^3]$

k : adsorbing rate constant $[mol^{(1-n)}/s \cdot m^{3(1-n)}]$

C : Mg concentration $[mol/m^3]$

n : adsorbing reaction order [-]

Figure 4 shows calculated Mg removal efficiency using the fitted adsorption equation, where n of adsorbing reaction order was fitted as 1, for the high-pressure condition. This means the phenomenon at the high pressure obeys common first-order adsorption kinetics. Data for the low-pressure mode were fitted as well with n = 1, but a mutually applicable adsorbing rate constant could not be obtained. For the low-pressure mode, k fit is more than 10 times larger than that for the high-pressure mode, which readily explains a majority of gel capture within the first media layer in Figure 3. As the apparent kinetic model (not intrinsic kinetics plus migration kinetics model) was applied, k contains the transportation effect, which plays a much more important role at high pressure, supporting the explanation noted in the previous section.

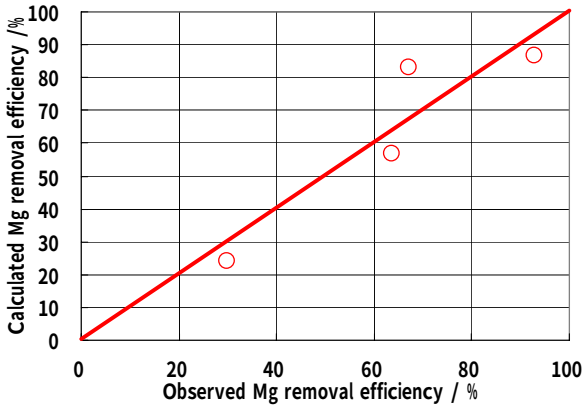

Figure 4. Calculated Mg Removal Efficiency for high-pressure filtration using fitted apparent adsorption rate equation.

4. CONCLUSION

Lower filtration pressure and longer contact time were found to enhance the removal of gel-like microbridge defect precursors during point-of-use filtration of photoresist polymer solution. A kinetic study of high-pressure filtration was performed in order to better understand the strong gel removal dependency on contact time. This study revealed the gel-like precursors are adsorbed to a greater extent at sites of the polar Nylon 6,6 throughout the membrane depth. Study of gel capture position within the depth of the filter media during low pressure filtration by ICP-MS, where there is no gel removal dependency on contact time, revealed the gels were captured at the inlet portion of the filter. This was due to the smaller transportation force into filter media depth under low pressure conditions.

These findings will be very useful both in optimizing filter operating procedures and in the development of next-generation filtration products, ultimately contributing toward reduced defectivity and increased yield within next-generation lithography processes.

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