Metal reduction at bulk chemical filtration

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ABSTRACT

OK73 thinner and cyclohexanone, both of which were spiked with metals were passed through Nylon 6,6 filter, varying flow rate, which include the conditions of both point-of-use and bulk filtrations. The influent and effluent metal concentrations were measured using ICP-MS for metal removal efficiency of the filtration. As a result, removal efficiency for some metals descended depending on the flow rate, while others maintained. Slower flow rate is recommended to maintain low metal concentration in bulk filtration based on the result. Metals in cyclohexanone were reduced at higher efficiency than in OK73 thinner, agrees with a metal removal model of hydrophilic adsorbent in organic solvent, evidenced in our previous paper. Further, metal reduction on 300 mm φ Si wafer after coating organic solvents with Nylon 6,6 filtration was evidenced with TRXF analysis.

Keywords: Metal reduction, Nylon 6,6, HDPE, PGME, PGMEA, Cyclohexanone, Bulk chemical filtration, TRXF

1. INTRODUCTION

Metal impurities are one of the major concerns that potentially deteriorates electronic performance of the semiconductor device[1] In our previous SPIE paper[2], we have demonstrated that Nylon 6,6 filtration is effective in removing metal impurities in organic solvents at point-of-use (POU) filtration and found that the removal efficiency depends on the hydrophobicity (octanol water partition coefficient, LogP) of the fluid. Also, we have identified that the metal is removed by means of partitioning to the water layer formed on the hydrophilic Nylon 6,6 membrane, similarly to the hydrophilic interaction chromatography, which precedes in mechanism identification on the hydrophilic interactions in organic solvents[3,4]. In bulk filtration at chemical suppliers, typical flow rate per unit filtration area is faster than that in the point-of-use filtration. This may adversely impact the metal removal efficiency. In the current work, we studied metal reduction as a function of flow rate per unit filtration area which includes both conditions in POU and in bulk chemical filtrations. Further, as a realistic experiment for the leading edge semiconductor device industry, metal analysis on 300 mm φ Si wafer was carried out after coating organic solvents with and without filtration.

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2. EXPERIMENTAL

2.1 Metal reduction in lithography solvents as a function of flow rate

Metal challenge solution was made by adding metal analytical standard (SPEX XSTC-622B) to the test solvents. Using the test stand shown in Figure 1, filtration was conducted under constant flow by adjusting inlet pressure while the flow rate is monitored. Influent and effluent metal concentrations were measured using a standard inductive coupled plasma mass spectroscopy (ICP-MS) analytical tool (Agilent 7700s).

OK73 thinner (7:3 mixture of propylene glycol monomethyl ether (PGME) and propylene glycol monomethyl ether acetate (PGMEA), TOK) and electronic grade cyclohexanone (Showa Denko) were used for the test fluid. The challenge concentration for each metal was 1 ppb. Pall 5 nm rated high flow asymmetric Nylon 6,6 membrane in 47 mm φ disk was the test filter. The test flow rate was varied from 0.04 to 0.74 $mL \cdot min.^{-1} \cdot cm^{-2}$ to include equivalent ones for both point-of-use filtration (lower side) and bulk chemical filtration (higher side).

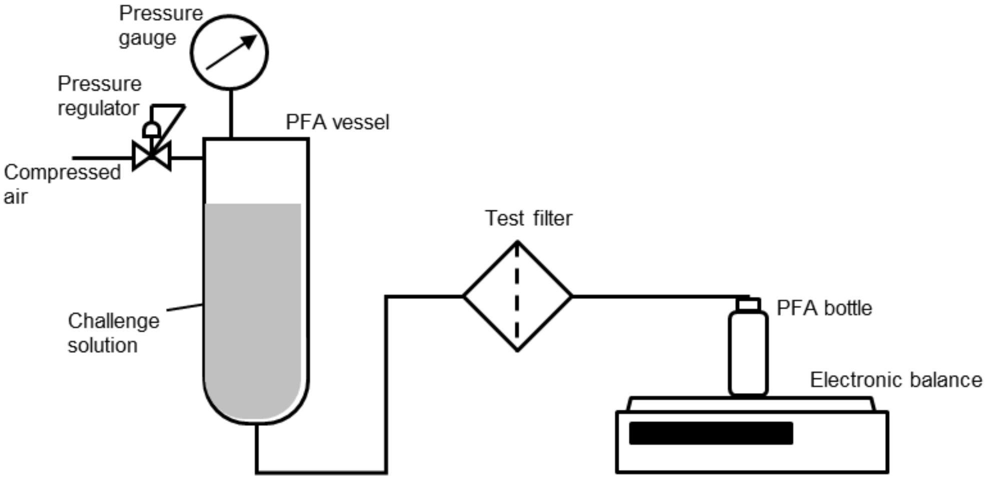

Figure 1. Test stand for metal challenge test.

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2.2 Metal amount on Si wafer after coating unfiltered and filtered metal spiked solvent

Sample preparation and TRXF analysis were performed by TOK. In a preliminary test, standard electronic grade test solvents made by TOK were found not to contain any detectable metals for the following test, consequently metal ion was intentionally added. Metal challenge solution was made by adding metal analytical standard (SPEX XSTC-622B) to the test solvents. Using the test stand shown in Figure 2, filtration was conducted under constant flow with a designated pressure that was measured beforehand to establish the test flow rate. Then as shown in Figure 3, the unfiltered and the filtered solvents were coated on 300 mm φ Si wafer and dried. Fe amount on the Si wafers were measured using total reflection x-ray fluorescence (TRXF, TREX 632III).

OK73 thinner (TOK) and electronic grade cyclohexanone (TOK) were used for the test fluid. The challenge concentration for each metal was 10 ppb. Pall PhotoKleen DDF filters with 5 nm rated high flow asymmetric Nylon 6,6 membrane and with 2 nm rated high flow high density polyethylene (HDPE) membrane were the test filters. The test flow rates per unit filtration area were 0.1, 0.3 and 0.5 $mL \cdot min.^{-1} \cdot cm^{-2}$. TRXF measurement was carried out for 49 points with each 10 mm φ spot.

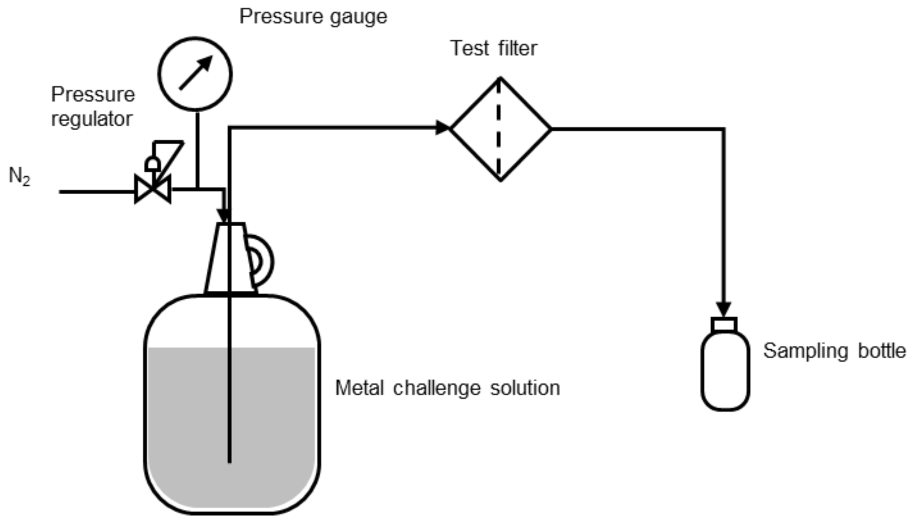

Figure 2. Test stand for metal challenge test for TRXF analysis.

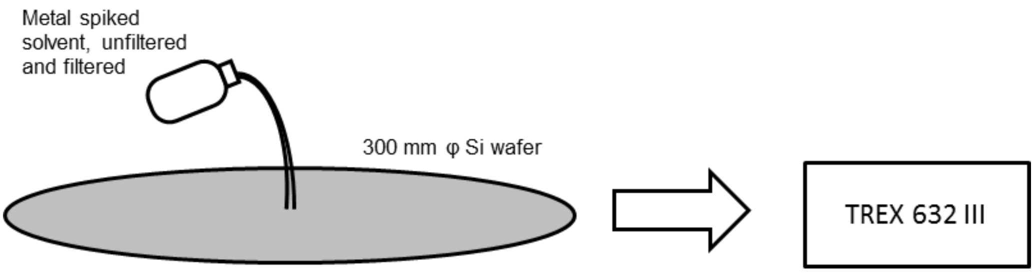

Figure 3. TRXF analysis on 300 mm φ Si wafer

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3. RESULTS AND DISCUSSIONS

3.1 Metal reduction in lithography solvents as a function of flow rate

3.1.1 OK73 thinner

As shown in Figure 4, the removal efficiency for some metals descended by increasing the flow rate from the one with POU to the one with bulk, while other metals maintained efficiency. For details, removal efficiency of Li, Co, Fe, Cr and Ni was reduced in the typical flow rate at bulk chemical filtration in comparison to the one at POU filtration. Removal efficiency of Mg, Ca and Mn maintained the same at high efficiency regardless of the flow rate. No significant reduction was found for Na and K.

Based on the result, flow rate per unit filtration area is found to be one of the key factors for reducing specific kinds of metal impurities in OK73 thinner. Flow rate reduction in the current filtration system, use of more and longer filter cartridges and use of filter with thicker membrane are the recommendations for the improvement.

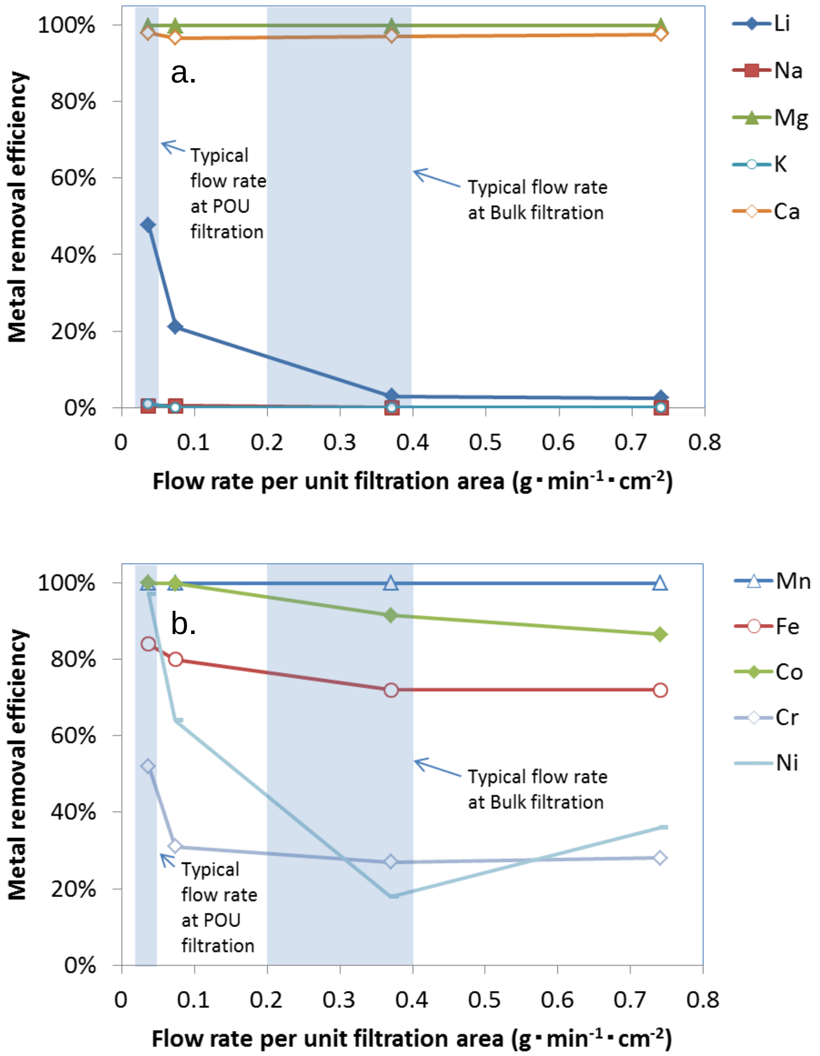

Figure 4. Metal removal efficiency in 5 nm rated high flow Nylon 6,6 membrane filtration for OK73 thinner as a function of flow rate per unit filtration area. a.: Li, Na, Mg, K and Ca, b.: Mn, Fe, Co, Cr and Ni. Each plot indicates average of two test runs.

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3.1.2 Cyclohexanone

As shown in Figure 5, the removal efficiency for some metals descended by increasing the flow rate from the one with POU to the one with bulk, while other metals maintained efficiency. For details, removal efficiency of Ca and Na was reduced in the typical flow rate at bulk chemical filtration. Removal efficiency of Li, Mg, Mn, Co and Cr maintained the same at high regardless of the flow rate. Removal efficiency of K maintained at moderate.

Overall, metals in cyclohexanone were reduced at higher efficiency than in OK73 thinner. This agrees with a metal removal model of hydrophilic adsorbent in organic solvent, which is evidenced in our previous paper[2]. In cyclohexanone, the driving force of the metal adsorption to the water layer formed on the Nylon 6,6 membrane was stronger than in OK73 thinner due to greater hydrophobicity of the cyclohexanone.

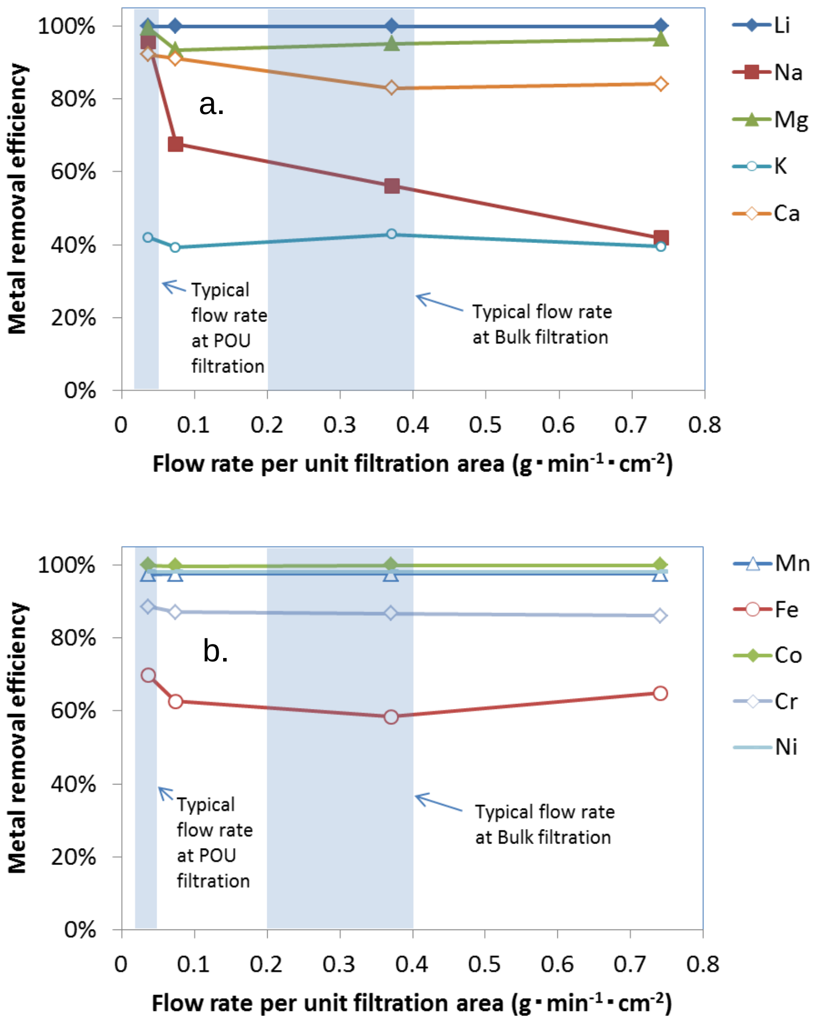

Figure 5. Metal removal efficiency in 5 nm rated high flow Nylon 6,6 membrane filtration for cyclohexanone as a function of flow rate per unit filtration area. a.: Li, Na, Mg, K and Ca, b.: Mn, Fe, Co, Cr and Ni. Each plot indicates average of two test runs.

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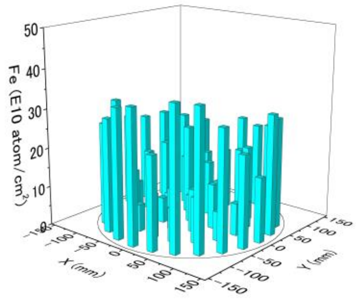
3.2 Metal amount on Si wafer after coating unfiltered and filtered metal spiked solvent

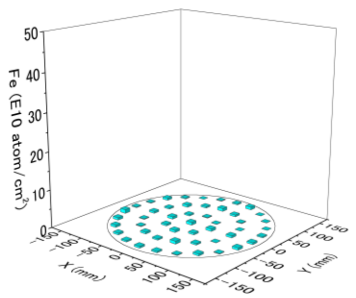
3.2.1 OK73 thinner

Effect of filtration for the metal reduction in organic solvents were evaluated on Si wafer. As shown in Figure 6, Fe amount on Si wafer coated with unfiltered metal spiked OK73 thinner was approximately 30 atom/cm^2. With 5 nm rated high flow Nylon 6,6 filtration, the metal level was reduced to <1 atom/cm^2. With HDPE filtration, metal amount on the Si wafer was not reduced.

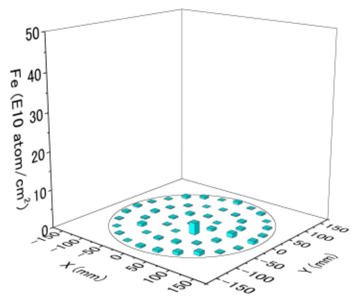
In the ICP-MS analysis results shown in Figure 4, Fe is rather stable in flow rate dependence in the range of 0.1 – 0.5 mL·min.$^{-1}$·cm^{-2}. The metal amount on the Si wafer behaved similarly.



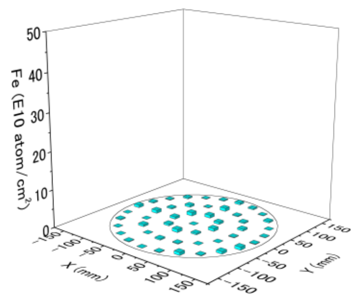
Unfiltered, 10 ppb metal spiked solvent



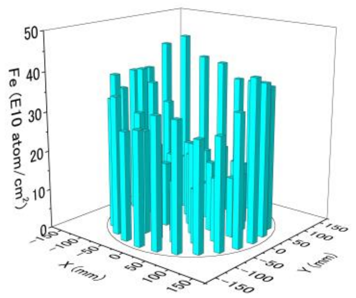
Filtered, N66, 0.1 mL·min.$^{-1}$·cm^{-2}



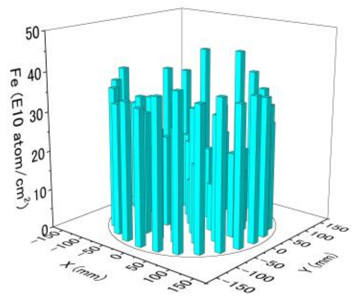
Filtered, N66, 0.3 mL·min.$^{-1}$·cm^{-2}



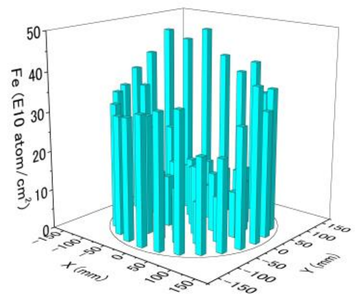
Filtered, N66, 0.5 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.1 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.3 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.5 mL·min.$^{-1}$·cm^{-2}

Figure 6. Metal (Fe) amount on Si wafer after coating metal spiked OK73 thinner, which was unfiltered and filtered with 5 nm rated high flow Nylon 6,6(N66) and 2 nm rated high flow HDPE membrane, as a function of flow rate per unit filtration area.

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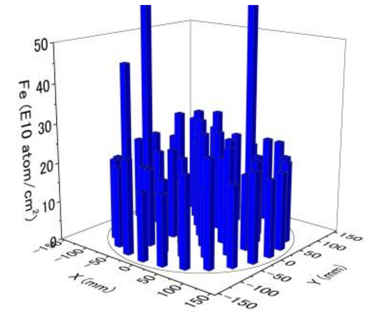
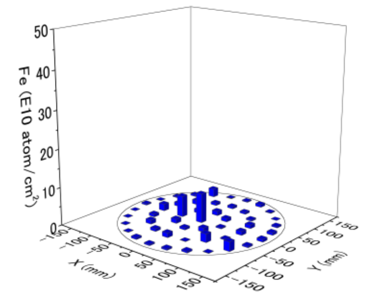
3.2.2 Cyclohexanone

As shown in Figure 7, Fe amount on a Si wafer coated with unfiltered metal spiked cyclohexanone was approximately 30 atom/cm^2 similar to OK73 thinner. With 5 nm rated high flow Nylon 6,6 filtration, the metal level was reduced to <1 atom/cm^2. And HDPE filtration was not effective for reducing metal.

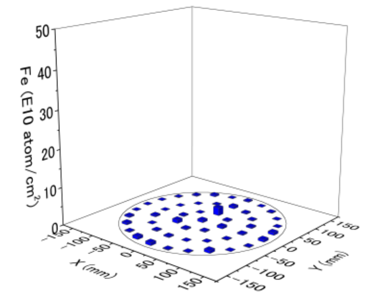
Similarly to OK73 thinner, Fe in cyclohexanone is rather stable in flow rate dependence in the range of 0.1 – 0.5 mL·min.$^{-1}$·cm^{-2}. The metal amount on the Si wafer behaved similarly.



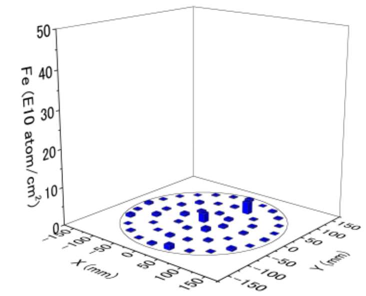
Unfiltered, 10 ppb metal spiked solvent



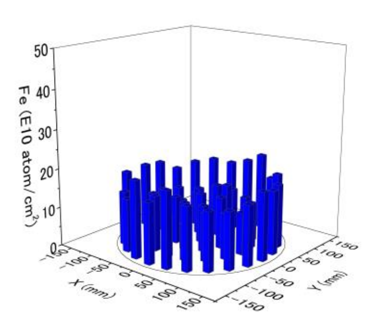
Filtered, N66, 0.1 mL·min.$^{-1}$·cm^{-2}



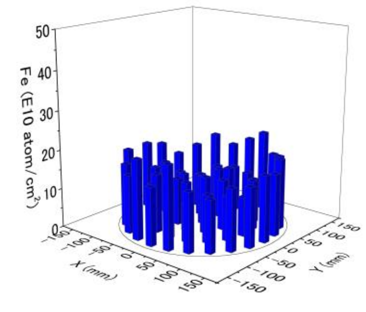
Filtered, N66, 0.3 mL·min.$^{-1}$·cm^{-2}



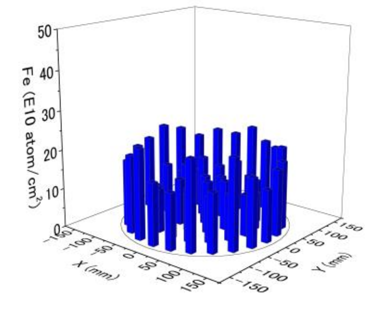
Filtered, N66, 0.5 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.1 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.3 mL·min.$^{-1}$·cm^{-2}



Filtered, HDPE, 0.5 mL·min.$^{-1}$·cm^{-2}

Figure 7. Metal (Fe) amount on Si wafer after coating metal spiked cyclohexanone, which was unfiltered and filtered with 5 nm rated high flow Nylon 6,6(N66) and 2 nm rated HDPE membranes, as a function of flow rate per unit filtration area.

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4. CONCLUSION

Flow rate per unit filtration area was found to be a key factor for effectively reducing metals in organic solvents using Nylon 6,6 filtration and a potential for improving metal removal efficiency in the bulk chemical filtration was also suggested from the results. The flow rate dependence was much significant in more hydrophilic solvent.

Further, as a real-world results for the leading edge semiconductor device industry, metal reduction on 300 mm φ Si wafer after coating organic solvents with Nylon 6,6 filtration was evidenced with TRXF analysis.

5. ACKNOWLEDGEMENT

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