

# Metal reduction at point-of-use filtration

Toru Umeda<sup>\*a</sup>, Shusaku Daikoku<sup>a</sup>, Rao Varanasi<sup>b</sup> and Shuichi Tsuzuki<sup>a</sup>

<sup>a</sup>Nihon Pall Ltd., 46 Kasuminosato, Ami-machi, Inashiki-gun, Ibaraki, Japan 3000315; <sup>b</sup>Pall Corporation, 25 Harbor Park Drive, Port Washington, NY USA 11050

## ABSTRACT

We explored the metal removal efficiency of Nylon 6,6 and HDPE (High Density Polyethylene) membrane based filters, in solvents of varying degree of polarity such as Cyclohexanone and 70:30 mixture of PGME (Propylene Glycol Monomethyl Ether) and PGMEA (Propylene Glycol Monomethyl Ether), In all the solvents tested, Nylon 6,6 membrane filtration was found to be significantly more effective in removing metals than HDPE membranes, regardless of their respective membrane pore sizes. Hydrophilic interaction chromatography (HILIC) mechanism was invoked to rationalize metal removal efficiency dependence on solvent hydrophobicity.

**Keywords:** Metal reduction, Nylon 6,6, HDPE, PGME, PGMEA, Cyclohexanone, HILIC

## 1. INTRODUCTION

As semiconductor manufacturing heads towards 1X nm pattern fabrication nodes, stringent requirements for metal reduction are being placed on lithography process chemicals. These requirements are due to concerns for deteriorating performance of the semiconductor device due to lithography process induced defects [1,2]. Although many lithography chemicals can be supplied with sufficiently reduced metal concentrations [3], the chemicals can also become contaminated by metal components in the flow path between the chemical delivery system and the Si wafer.

Ion-exchange filters are typically used for metal reduction in semiconductor process fluids. These filters make use of strong acid ion-exchange groups which provide good metal removal efficiency and high ion-exchange capacity [4]. However, ion exchange groups also have a tendency to adsorb the ionic additives such as quenchers and onium salts (ionic photoacid generators) present in chemically amplified photoresists (CAR). For this reason, ion-exchange filters are less suitable for lithography formulations which need to be filtered for metal and particle contaminations prior to spin coat them on Si wafers in lithographic process tracks.

In this study, we explored the metal removal efficiency of Nylon 6,6 and high density polyethylene (HDPE) membrane based filters, in solvents of varying degree of polarity such as Cyclohexanone and 70:30 mixture of Propylene glycol methylether (PGME) and Propylene glycol methylether acetate (PGMEA).

Further, mechanism of metal reduction by Nylon 6,6 membrane is explored. Similarly to the current study, hydrophilic-interaction chromatography (HILIC) utilizes adsorption in organic solvent. Present theory proposes that HILIC retention is caused by partitioning between hydrophobic solvent and a layer enriched with water and partially immobilized on the adsorbent, but is not direct retention by adsorbent [5]. Alpert evidenced this by performing HILIC of polar compounds in various proportion of water-organic solvent mixture, resulting higher adsorption efficiency in both charged (cation exchanger) and uncharged hydrophilic adsorbent at higher organic solvent content for both positively and negatively charged amino acids[6]. We conducted a similar experiment on hydrophilic Nylon 6,6 filter for metal ion retention to verify whether the same mechanism can be applied. This was also performed on cation exchange filter.

\*toru\_umeda@ap.pall.com; phone 81 90 7837-4574; fax 81 29 889-1957

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## 2. EXPERIMENTAL

### 2.1 Metal reduction in lithography solvents

First the metal challenge solution was made by adding 1 ppb of metal analytical standard (SPEX XSTC-622B) to the test solvent. Using the test stand shown in Figure1, filtration was conducted under steady flow by adjusting inlet pressure while monitoring the flow rate of 0.5 ml/sec which is common in lithography solvent dispense systems. Influent and effluent metal concentrations were measured using a standard ICP-MS analytical tool (Agilent 7700s). Pall PhotoKleen\* EZD-3X filter with 5 nm rated Nylon 6,6 and 2 nm rated HDPE were used for the test filters.

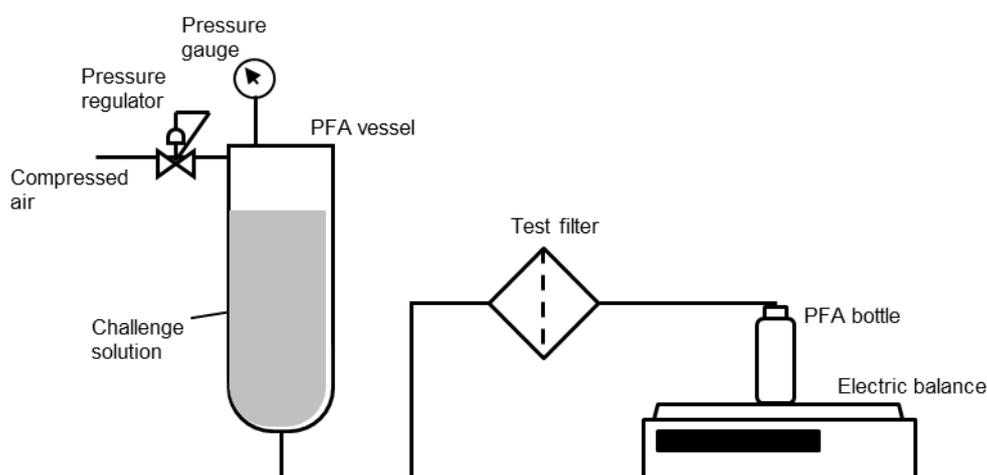


Figure1. Test stand for metal challenge test.

### 2.2 Mechanism investigation

The same procedure was used for the mechanism investigation on metal reduction in organic solvents. Using the test stand shown in Figure1, metal reduction as a function of solvent hydrophobicity on the 5 nm rated Nylon 6,6 and strong cation exchange filters were examined. The various hydrophobicity of the solvents were provided by using solvent/deionized (DI) water mixture and using multiple kind of solvents. In particular, PGME/DI water mixture with PGME fraction in 0, 25, 50, 75 and 100%, 70:30 mixture of PGME and PGMEA, 100% Cyclohexanone and 100% n-butylacetate were used. The test flow rate per unit filtration area was 0.03-0.04 ml/min./cm<sup>2</sup>.

\*: PhotoKleen is a trademark of Pall Corporation.

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### 3. RESULTS AND DISCUSSIONS

#### 3.1 Metal reduction in lithography solvents

The results are shown in Figures 2 and 3. In both of the solvents tested, Nylon 6,6 membrane filtration was found to be significantly more effective in removing metals than HDPE membranes, regardless of their respective membrane ratings.

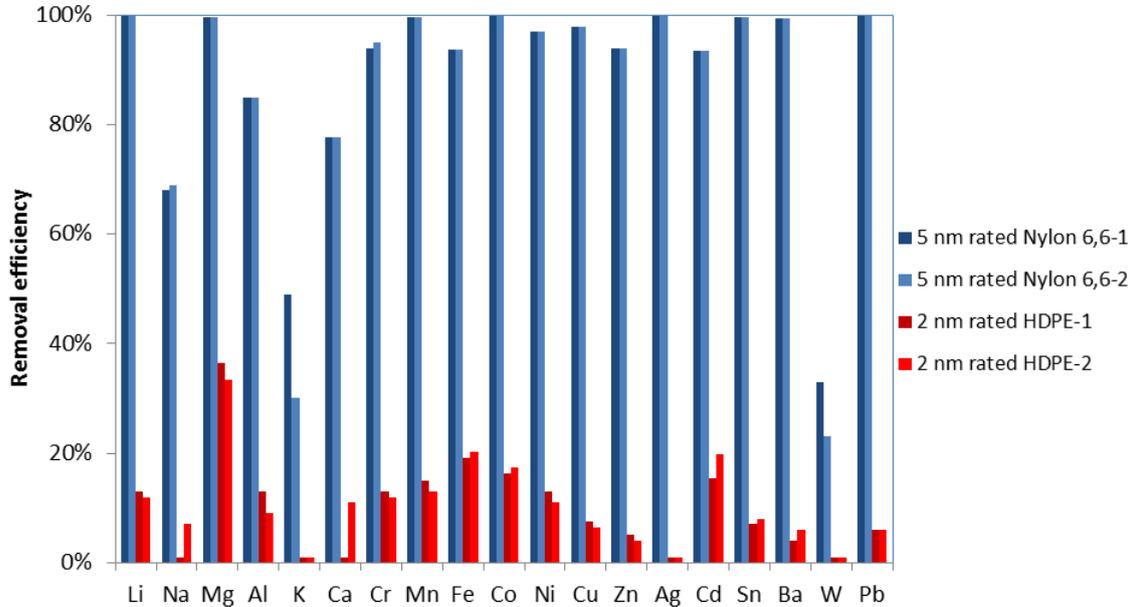


Figure 2. Metal removal efficiency of point-of-use filters in 70:30 mixture of PGME and PGMEA. -1 is 100-200 ml and -2 is 200-300 ml in throughputs. 0% is represented as 1% to differentiate with no data.

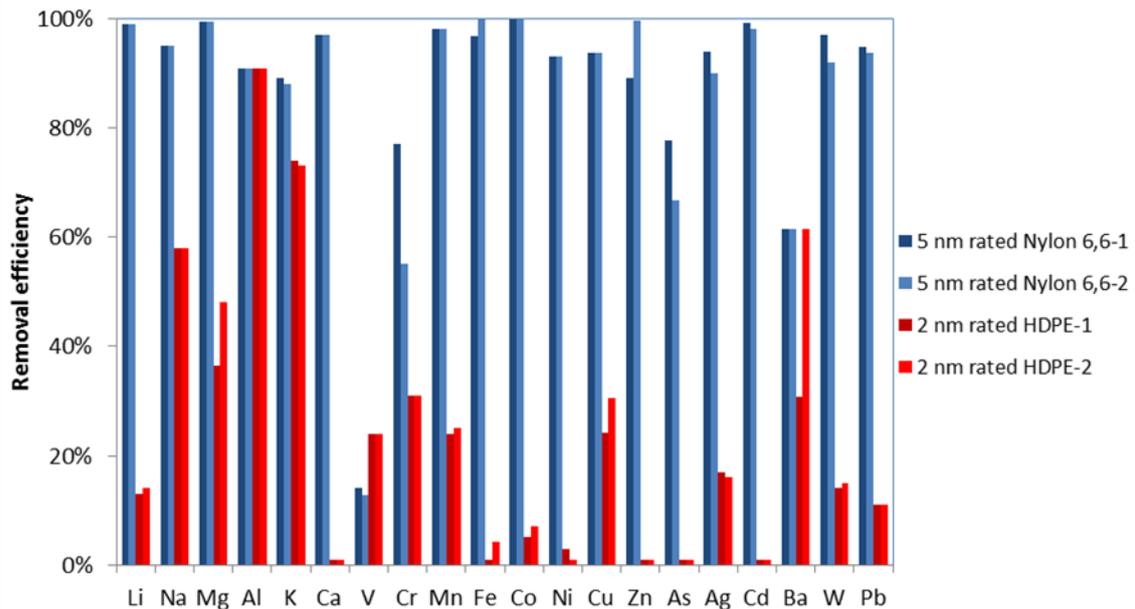


Figure 3. Metal removal efficiency of point-of-use filters in Cyclohexanone. -1 is 100-200 ml and -2 is 200-300 ml in throughputs. 0% is represented as 1% to differentiate with no data.

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### 3.2 Mechanism of metal reduction by Nylon 6,6 and ion exchange filters

Figure 4 shows metal removal efficiency as a function of solvent hydrophobicity (LogP). With Nylon 6,6 filter (Fig.4, right), both cation ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ) and anion ( $\text{WO}_4^{2-}$ ) are not retained in the absence of organic solvent (LogP=-1.38). A significant increase in retention of the ions regardless the charge is found as the hydrophobicity of the solvent is increased. This suggests that both cation and anion are partitioned in the thin aqueous layer formed around the polar sites (CONH bonds and  $-\text{NH}_2$ ,  $-\text{COOH}$  end groups) of Nylon 6,6 filter, as shown in Figure5. This is similar on ion exchange filter (Fig.4, left), but is superimposed on ion exchange effect. Even in absence of organic solvents, cations are well retained. Anion is not retained in the absence or at low levels of organic solvent, indicating electrostatic repulsion. This is also evidenced by the lower removal efficiency than Nylon 6,6 filter throughout all the LogP range. These essentially resemble well the results by Alpert, indicating that the mechanism proposed in HILIC can be applied with metal reduction in organic solvents using Nylon 6,6 and ion exchange filters.

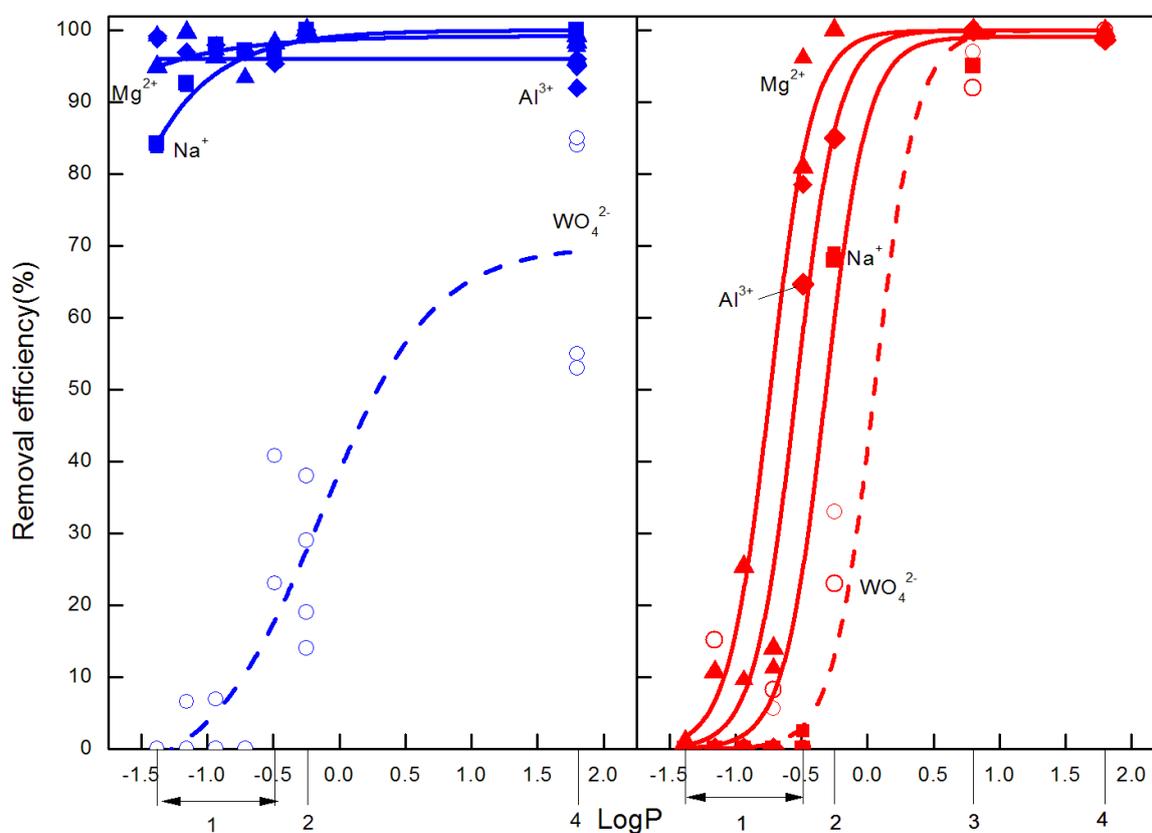


Figure 4. Metal removal efficiency in filtration as a function of octanol-water partition coefficient (LogP) of the solvents. 1: PGME-DI water mixture; PGME 0, 25, 50, 75 and 100%, 2: 70:30 mixture of PGME and PGMEA, 3: Cyclohexanone and 4: n-Butylacetate. LogP of the solvent mixture is determined by mass fraction of the two individual solvents. Ionic form of the metals are determined based on the ingredient chemical compounds for the standard metal solution. Left: Cation exchange filter, Right: 5 nm rated Nylon 6,6 filter.

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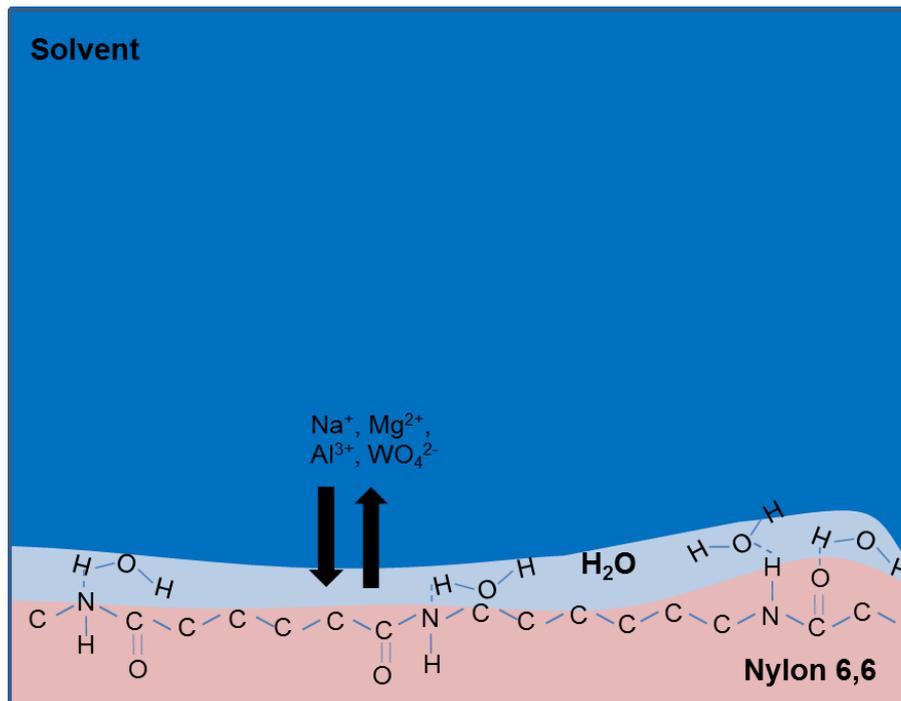


Figure 5. Scheme of the metal ion adsorption mechanism on Nylon 6,6 filtration. The concept is based on HILIC mechanism [5].

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#### 4. CONCLUSION

In 70:30 mixture of PGME and PGMEA and Cyclohexanone, Nylon 6,6 membrane filtration was found to be significantly more effective in removing metals than HDPE membranes, regardless of their respective membrane pore sizes.

For mechanism investigation, a partitioning model, which resembles the HILIC, is evidenced by metal removal efficiency dependence on solvent hydrophobicity.

Based on the results, Nylon 6,6 filtration is recommended for metal reduction in lithography process solvents such as 70:30 mixture of PGME and PGMEA, and Cyclohexanone, in which metal impurities are strictly required to be reduced towards making 1X nm patterns.

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