Application specific ratings for lithography process filters

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ABSTRACT

The typical performance index of microelectronics-grade filter products is based upon mechanical sieving. However, adsorption also plays a critical role for reducing certain defects. To provide a more accurate metric, a complementary adsorption performance index is introduced for lithography process filters. In this study, heptylamine-substituted palladium nanoparticles were used to simulate the adsorptive characteristics of microbridge defect precursors. Adsorption kinetic parameters were calculated for Nylon 6,6 and HDPE filters that were challenged with the simulation particles. Nylon 6,6 media quantitatively demonstrated superior adsorptive retention characteristics. The new index is expected to guide both filter product development and filter recommendation for next generation lithography processes.

Keywords: Adsorption, Quantification, Filtration, Nylon 6,6, Palladium, Nanoparticle, Microbridge

1. INTRODUCTION

Typically, the performance index of microelectronics-grade filter products is described in dimensions of particle removal rating, such as “20 nm” or “0.03 µm.” These ratings describe a sieving mechanism for removal of classical hard particles from an aqueous colloidal system[1]. In actual application, adsorptive mechanisms certainly play a critical role in contaminant filtration. Especially, it was repeatedly confirmed that DUV resist filtration using adsorptive Nylon 6,6 membrane significantly reduces microbridge defects within the lithography process[2-6]. Continual progress in litho technology is driving requirements both for enhanced effectiveness and for greater understanding of filtration mechanisms. Thus, a need has been identified for an adsorption performance index that will complement the familiar filter removal ratings, and will help to more accurately develop and recommend next generation lithography (NGL) filter products for NGL fluids. In this paper, method development of an adsorption performance index targeted at DUV and EUV applications is described.

2. OVERALL WORKFLOW

The overall workflow for the application specific ratings is summarized in Figure 1.

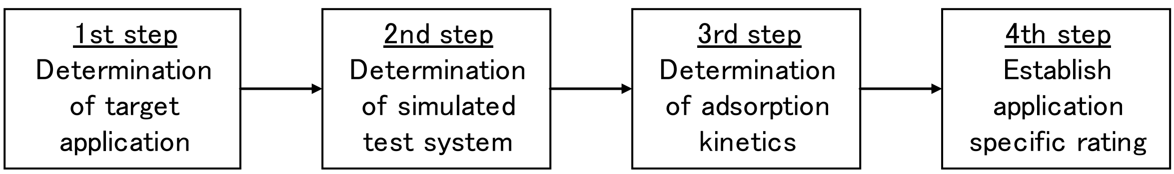

Figure 1. Schematic of overall workflow for application specific rating.

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The first step of the work is to determine a target application. Simulated filtration setting for adsorptive evaluation should be customized with respect to each target application because, as shown in Figure 2, ①defect sources – filter media interaction is not the only one that should be considered, ②but solvent – filter media interaction and ③defect sources – solvent interaction also affect effluent quality.

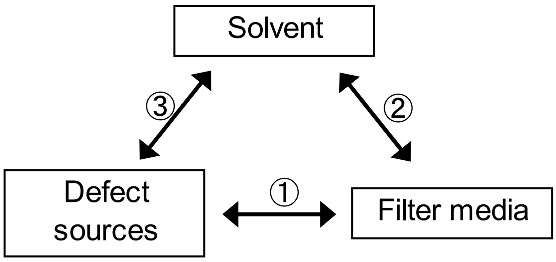

Figure 2. Schematic of interactions among elements in a liquid filtration system[7].

The second step is to determine a simulated filtration test system that simulates the target application. Many solvents and filter media materials are commercially available for testing; however, defect sources are not, due to difficulties in identification and procurement. Instead, simulation particles were developed with regard to the characteristics identified within known defect sources. Then, adsorption performance in the simulated filtration system was quantified as the third step and finally, using the determined adsorption rate parameters, an adsorptive performance index (application-specific rating) was calculated.

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3. TARGET APPLICATION

DUV and EUV lithography are the target applications for the current work.

4. SIMULATING A TEST SYSTEM

4.1 Solvent

Propylene glycol mono methyl ether acetate (PGMEA) was selected as a test solvent because this is a common and widely used solvent in DUV and EUV photolithography process fluids.

4.2 Target defect

Microbridge precursors are the targeted defect source, because of their relevance and potential impact on DUV[2-6] and EUV litho processes[8,9]. As shown in Figure 3, microbridge reduction by filtration is more sensitive to membrane material than to membrane removal [5]. This is assumed to be due to aggregated gel of hydrophilic and low-solubility polymer fraction being adsorbed onto hydrophilic amide bonds of the Nylon 6,6 membrane. This property was used to select the simulation particle.

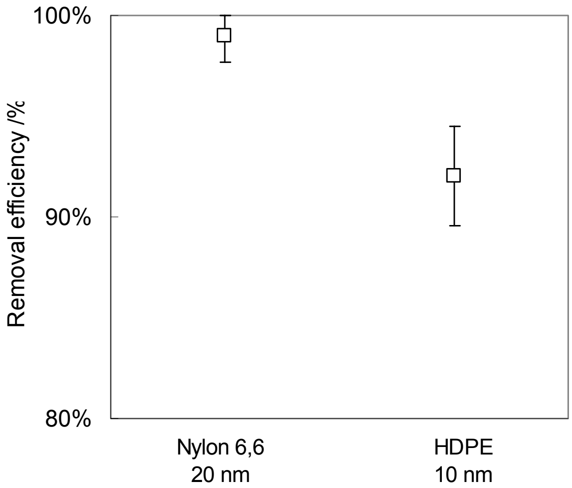

Figure 3 Microbridge removal efficiency* in 193 nm lithography[5] (L/S 90 nm hp). Resist solvent: PGMEA *: Removal efficiency = 1 - (microbridge defect density on wafer with test filter)/(microbridge defect density on wafer with dummy capsule). Typical flow rate of the photoresist point of use filtration is 0.5 ml/sec.

4.3 Metal nanoparticles

To evaluate adsorption property of a filtration product, properties of a simulation particle that would be expected are adsorption similar to practical defect precursors, and minimized sieving, in order to exclusively evaluate adsorption. Metal nanoparticles are composed of a core metal particle and a ligand, which determines adsorptive properties. Metal nanoparticles are optimal for this study because sieving can be minimized by using sufficiently small particles and adsorption can be simulated by using ligands that possess adsorption characteristics similar to those of defect precursors.

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4.4 Sieving contribution of metal nanoparticles

Before selecting ligands to match adsorptive properties of microbridge defect precursors, sieving retention of the metal nanoparticle core was verified via challenge testing. As described, adsorption performance in filtration is affected by all interactions within the test system, whereas sieving is influenced by the relative sizes of test particles and filter membrane pores. To evaluate sieving exclusively, ligands and solvents were selected such that adsorptive interactions were minimized, based on a previous study[10]. Samples evaluated were flat sheet membrane disks (47 mm diameter). Results shown in Table 1 indicate that the membranes tested did not remove the 3 - 4 nm nanoparticles by sieving effect. In addition, lower sieving performance of Nylon 6,6 40 nm compared to Nylon 6,6 20 nm was confirmed in a previous study[1].

Table 1. Sieving contribution of the metal nanoparticles.

Membrane	Nanoparticle / size	Solvent	Removal efficiency
HDPE 10 nm	Pd-Heptylamine / 4 nm	Cyclohexanone	0%
HDPE 30 nm	Pd-Heptylamine/ 4 nm	Cyclohexanone	0%
Nylon 6,6 20 nm	Au-Hexanethiol /3 nm	PGMEA:PGME 95:5	0%

4.5 Selection of simulation metal nanoparticles[11]

Greater adsorptive retention of microbridge precursors in PGMEA-based solution by Nylon 6,6 membrane versus HDPE membrane has been consistently observed within the target application. To find particles which simulate such defect precursors, challenge testing in PGMEA with various liganded metal nanoparticles was conducted. Test filters were 47-mm diameter disks of 20 nm and 40 nm rated Pall asymmetric Nylon 6,6 membranes, and 10 nm and 30 nm rated Pall HDPE membranes. Inlet concentration of metal nanoparticles was 0.5 ppm and test flow rate was 5 ml/min. Results given in Figure 4 show that alkylamine-ligand-substituted nanoparticles were adsorbed on Nylon 6,6 to a greater extent than on HDPE, similar to microbridge defect precursors in DUV resists, which was shown in Figure 3. Also, reduction of alkyl chain length correlated to decreased ligand adsorption, especially on HDPE membranes, further enhancing the contrast between the membrane materials that can be used to improve the resolution of the experiment. A schematic of the assumed adsorption model is shown in Figure 5. Polar interactions between hydrophilic amide bonds on Nylon 6,6 and amine groups on the ligand were assumed to induce adsorption, similar to adsorption of defect precursors on Nylon 6,6.

Based on the results, Pd-Heptylamine was selected as a simulation particle for the target application.

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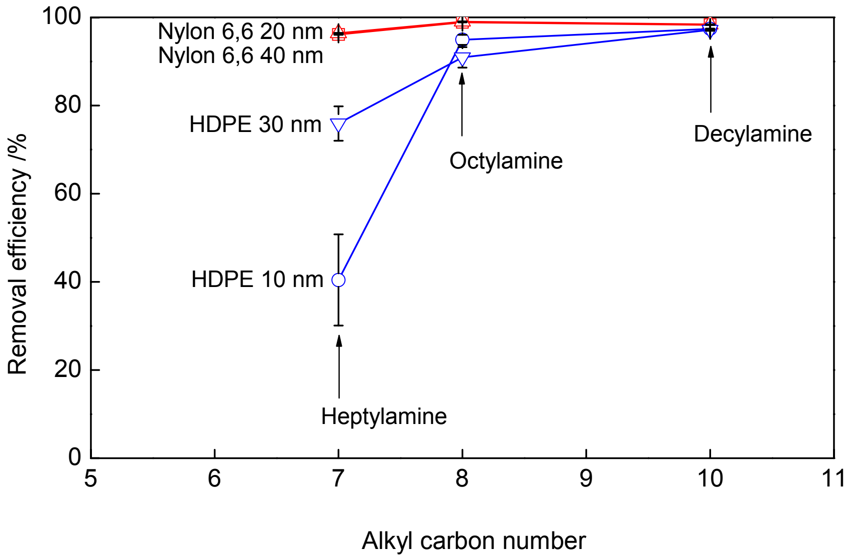

Figure 4 Pd nanoparticle removal efficiency as a function of ligand alkyl carbon number in nylon 6,6 and HDPE membrane filtration[11]

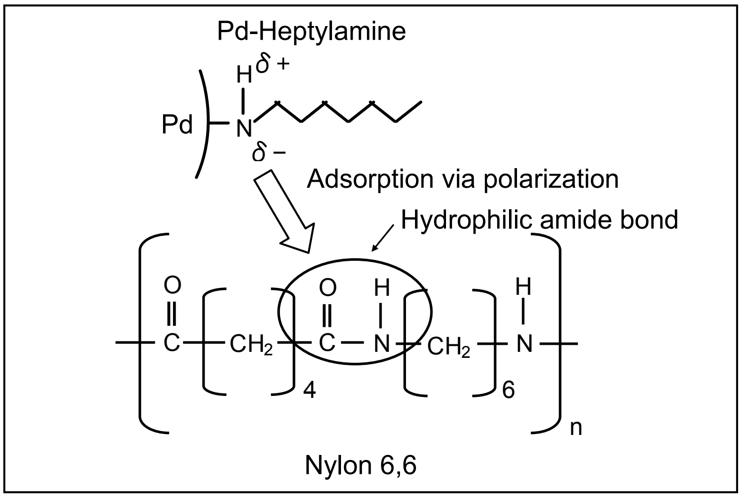

Figure 5 Schematic of polar interaction between amine in heptylamine ligand and amide bond on Nylon 6,6.

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5. ADSORPTION PARAMETER DETERMINATION

5.1 Model equation

n^{th}-order adsorption of an equilibrium process can be described as equation (1).

$$-\frac{d(C - C_E)}{dt} = k(C - C_E)^n \tag{1}$$

where C = adsorbent concentration, t = contact time between adsorbate and adsorbent, k = adsorption rate constant, n = adsorption reaction order, and C_E = adsorbent equilibrium concentration. Contact time dependence of metal nanoparticle removal efficiency during filtration of simulation particles is fitted to the above model equation in order to determine adsorption kinetics parameters n, k, and C_E. Contact time is described as equation (2).

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

5.2 Test method

Using a pressurized flow filtration test stand shown in Figure 6, contact time dependence of Pd-Heptylamine removal efficiency was evaluated. Contact time was varied by changing test flow rate. Test filters were 40 nm rated Pall asymmetric Nylon 6,6 membrane and 30 nm rated Pall HDPE membrane. The range of contact times tested was confirmed to include actual point of use resist filtration conditions that are employed in modern manufacturing processes. Challenge concentration was determined to be 0.5 ppb, based on the estimated gel concentration in a previous study[5]. 0.5 ppb Pd-Heptylamine in PGMEA was prepared by diluting stock solution (300 ppm Pd-Heptylamine in toluene, Tanaka precious metal) with PGMEA (Showa Denko EL grade). Filtration was conducted under steady flow by adjusting inlet pressure while monitoring flow rate. For both membrane types, one membrane sample was used to generate data at various contact time values. For each contact time value, the initial 10 g (10.4 ml) of effluent was discarded in order to displace fluid downstream of the test membrane, and then the next 10 g of effluent was sampled. Pd concentrations in the influent and effluents were measured using an Agilent 7700s ICP-MS. SPEX PLPD3-2Y palladium standard was used to prepare a calibration curve for quantitative analysis.

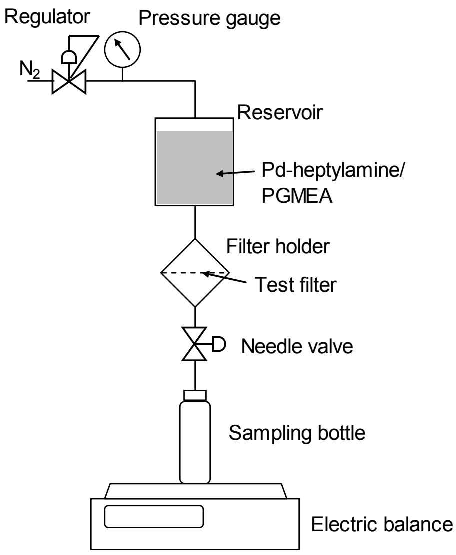

Figure 6 Pressurized flow filtration test stand.

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5.3 Determined adsorption parameters

Figure 7 shows Pd-Heptylamine (4 nm diameter) nanoparticle removal efficiency in PGMEA as a function of contact time (plots), and adsorption kinetics functions (lines) fitted using equation (1) with Origin 7.5 software. As a result, the determined adsorption kinetics parameters were: k = 111 [$ppb^{(1-n)}/s$], n = 1 [-], C_E = 0.02 [ppb] for Nylon 6,6 40 nm rated membrane, and k = 8.9, n = 1.8, C_E = 0.13 for HDPE 30 nm rated membrane. These parameters quantitatively indicate that adsorption of Nylon 6,6 is faster and shows greater removal efficiency at equilibrium.

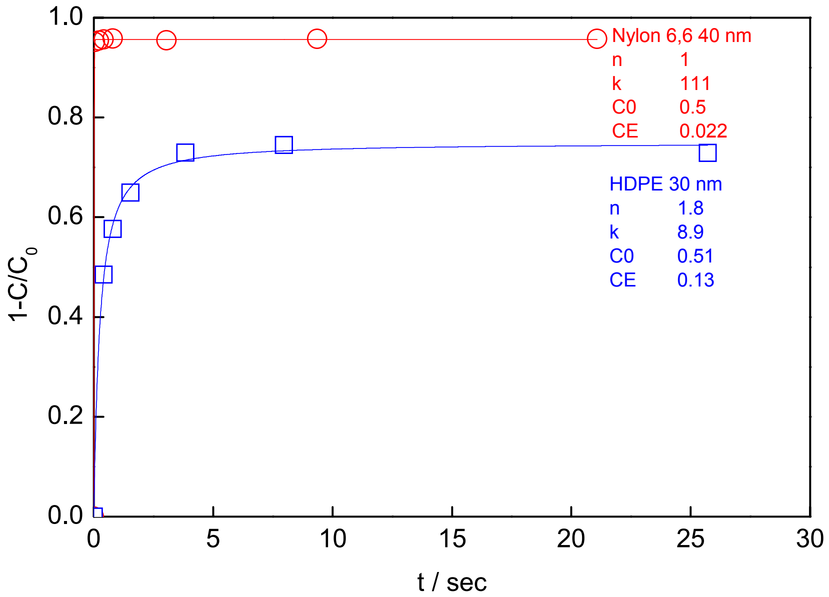

Figure 7. Contact time dependence of simulation particle removal efficiency ($1-C/C_0$) for Nylon 6,6 40 nm and HDPE 30 nm filters. Continuous lines are fitted adsorption rate equations. Simulation particle is Pd-Heptylamine (4 nm). Solvent is PGMEA. C_0 ~ 0.5 - 0.51 ppb.

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6. APPLICATION SPECIFIC RATINGS

It is desired to convert adsorption parameters into more intuitive, understandable metrics. Removal efficiency at a common resist dispensing condition is one candidate metric, as shown in Figure 8. Y-axis is calculated equilibrium removal efficiency, which represents adsorption performance, for a Pall PhotoKleen™ EZD-2 filter at a filtration rate of 0.5 mL/s. X-axis is filter ratings, which represents sieving performance. The graph indicates greater adsorption performance from the Nylon 6,6 filter.

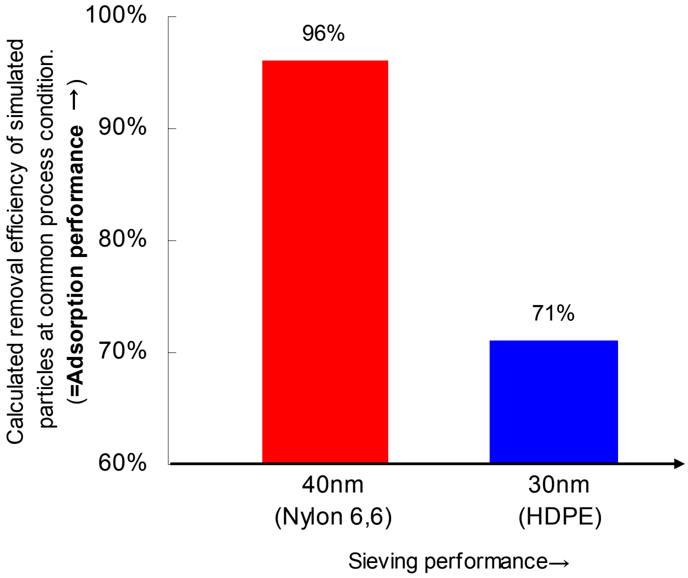

Figure 8. Adsorption and sieving performances of filter products. Adsorption performance is based on adsorption parameters determined by simulation particle filtration testing. Sieving performance is expressed as the established removal rating.

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7. CONCLUSION

An adsorption filtration performance index for lithography applications was developed using ligand-substituted metal nanoparticles. Removal rating evaluations that include the adsorption index are expected to more accurately reflect filter performance within actual photolithographic processes. A compilation of simulation particle challenge test results under various conditions, which considers all filter media, solvent, and defect source interactions, will provide both guidance for next-generation filter development and more effective prognostic recommendation of filter products for NGL processes.

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