Adsorption characteristics of lithography filters in various solvents using application-specific ratings

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ABSTRACT

It is known that DUV resist filtration using Nylon 6,6 membrane significantly reduces microbridge defects. Previous work has described a method to determine an adsorption performance index using modified metal nanoparticles, which simulate interactions with microbridge defect precursors. In this paper, the effects of filter grade, filter material, and solvent type on adsorptive retention are explored. The adsorption rate in Nylon 6,6 40 nm filter was observed to be greater in both lower-LogP_{ow} and lower-viscosity solvents, possibly providing a direction for improved filtration performance based on the solvent properties. The complementary adsorption kinetics parameters give a more accurate suggestion for the filter performance in lithography applications combined with the conventional sieving filter ratings.

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

1. INTRODUCTION

It is known that DUV resist filtration using adsorptive Nylon 6,6 membrane significantly reduces microbridge defects within the lithography process[1-5]. Also, a need has been identified for an adsorption retention performance index that will complement the familiar filter removal ratings that are currently used for microelectronics-grade filter products, which describe sieving retention performance by removal of classical hard particles from an aqueous colloidal system[6].

Previous work has described a method to determine an adsorption performance index for lithography process filters[7]. Using this metrology method, adsorption characteristics of a filter that is challenged with modified metal nanoparticles, which simulate interactions with microbridge defect precursors, is quantitatively determined in the form of kinetics parameters. In this paper, the effects of filter grade, filter material, and solvent type on adsorptive retention are explored. Further, the relationship between adsorption kinetics parameters and solvent properties are discussed.

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2. EXPERIMENTAL

2.1 Metal nanoparticle challenge testing

The adsorption performance index determination method developed in the previous study was employed[7]. In the method described above, the filter was challenged with microbridge surrogated metal nanoparticles with varying contact time* to determine the adsorption kinetics. Figure 1 illustrates the test stand employed.

*: Contact time (sec.) = Filter area (cm^2) × Filter thickness (cm) / Flow rate (cm^3/sec.)

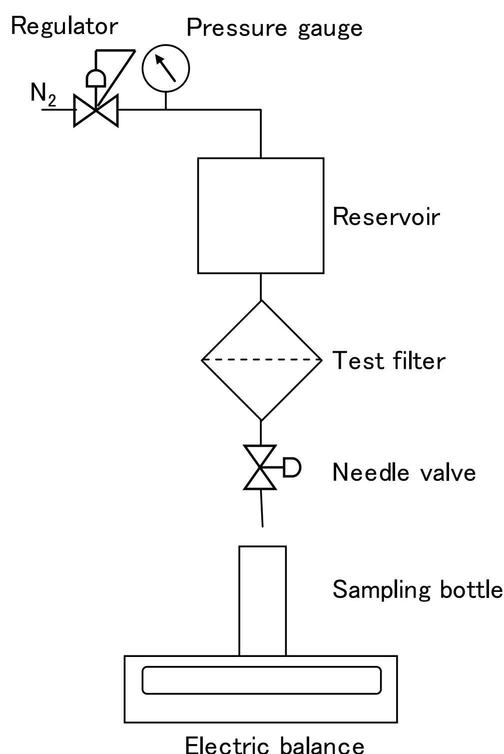

Figure 1. Schematic of filtration test stand employed for adsorption kinetics experiment.

The test filters were 47 mm diameter disks of 10, 20 and 40 nm rated asymmetric Nylon 6,6, Nylon 6,6 with extended contact time ('extension') and 30 nm rated high density polyethylene (HDPE). The test fluids were propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, n-butylacetate (n-BA) and gamma butyrolactone (GBL), all of which were selected as common lithography solvents and to compare solvent property to the adsorption kinetics. The solvent properties are listed in Table 1. Heptylamine-substituted palladium nanoparticles (Pd-HA), which were selected to simulate microbridge precursors, were used as challenge particles. The diameter of the Pd core was 4 nm. Preliminary testing with minimized adsorptive condition showed that all the test filters were not capable of retaining this size of nanoparticles by sieving. Therefore, the results in this paper exclusively indicate adsorption performance. The Pd-HA concentration in the influent was 0.5±0.025 ppb. Flow rate was controlled to vary contact time. The Pd concentration in the influents (=C_0) and the effluents (=C) were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS), to calculate removal efficiency (=1-C/C_0)

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Table 1 List of solvents and their properties used for adsorption kinetic study

	PGMEA	Cyclohexanone	n-BA	GBL
Log P_{ow}*	0.3	0.8	1.8	-0.76
Viscosity / mPas	1.3	2.2	0.94	1.7

*Log P_{ow}: Octanol-water partition coefficient, which indicates hydrophobicity (Greater values indicate increased hydrophobicity),

2.2 Adsorption kinetics

Adsorption kinetics at equilibrium are described by equation (1).

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

Where C=adsorbent concentration, t=contact time, k=adsorption rate constant, n=adsorption reaction order, and C_E=equilibrium concentration.

Differential equation (1) was solved for Pd removal efficiency values (= $1-C/C_0$) and is described by equation (2).

$$1-\frac{C}{C_0}=1-\frac{1}{C_0}\left\{(n-1)kt+(C_0-C_E)^{(1-n)}\right\}^{\{1/(1-n)\}}-\frac{C_E}{C_0} \qquad (2)$$

Pd removal efficiency values (= $1-C/C_0$) were fitted to Eq. (2) using Origin 7.5 data analysis software in order to determine adsorption kinetics parameters k and C_E. A second-order relationship (n = 2) was modeled using the results.

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3. RESULTS AND DISCUSSIONS

3.1 Adsorption kinetics

Figure 2 shows the results from various filters in PGMEA. The kinetics parameters in cyclohexanone, n-BA, and GBL were also determined with the same procedure. Adsorption rate constants, k, and equilibrium concentrations, C_E for all the test solvents were determined and are compiled in Tables 2, 3, 4, and 5..

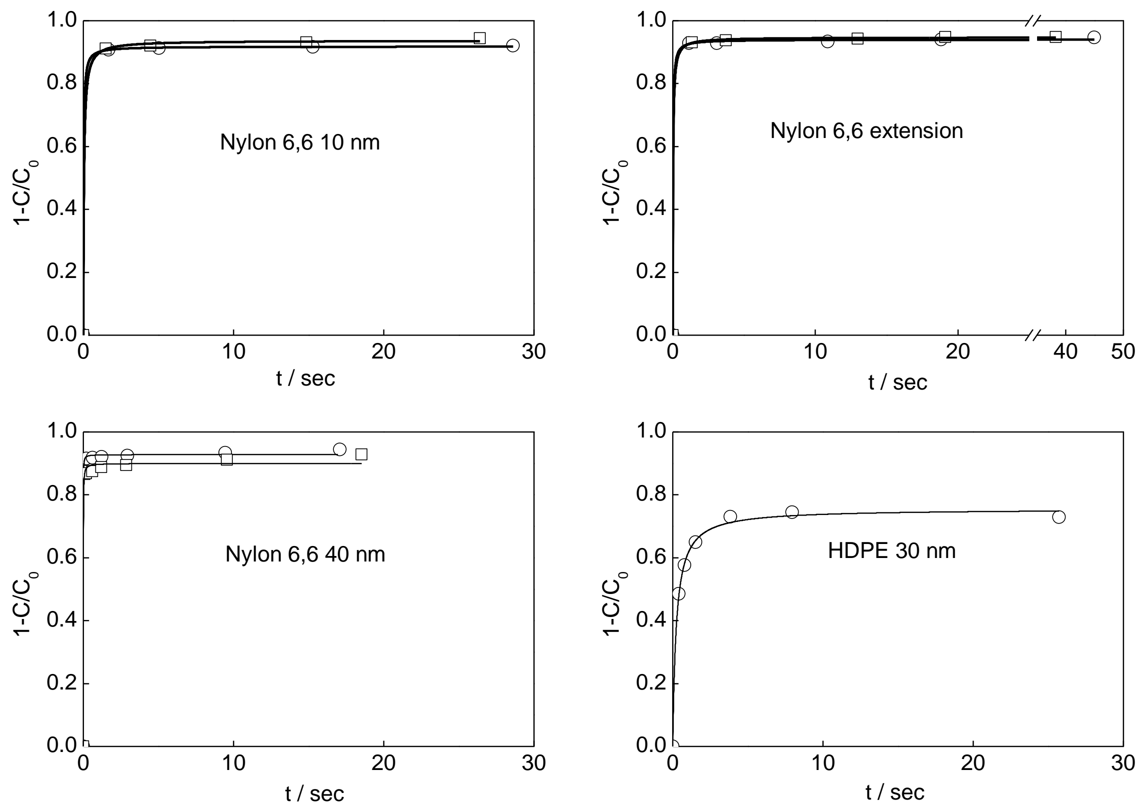

Figure 2. Contact time dependence of simulation particle removal efficiency (1-C/C_0) for various filters in PGMEA. Continuous lines are fitted adsorption rate equations. Simulation particle is Pd-Heptylamine (4 nm). C_0 ~ 0.49 - 0.52 ppb.

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Table 2. 2nd-order kinetics parameters determined by fitting kinetic-related data to Eq. (2) in PGMEA. r^2 is coefficient of determination.

Membrane	Test run	k / ppb$^{(1-n)}$*sec.$^{-1}$	C_E / ppb	r^2
Nylon 6,6 10 nm	1	1.1×10^2	0.040	0.99998
	2	52	0.031	0.99979
Nylon 6,6 extension	1	1.2×10^2	0.031	0.99982
	2	79	0.027	0.99997
Nylon 6,6 40 nm	1	1.4×10^3	0.037	0.99937
	2	6.4×10^2	0.051	0.99738
HDPE 30 nm	1	11	0.12	0.99786

Table 3. 2nd-order kinetics parameters determined by fitting kinetic-related data to Eq. (2) in cyclohexanone. r^2 is coefficient of determination.

Membrane	Test run	k / ppb$^{(1-n)}$*sec.$^{-1}$	C_E / ppb	r^2
Nylon 6,6 10 nm	1	3.1×10^2	0.028	0.99981
	2	19	0.028	0.99997
Nylon 6,6 extension	1	8.0	0.03	0.99978
	2	23	0.021	0.99994
Nylon 6,6 20 nm	1	94	0.019	0.99999
	2	52	0.027	0.99999
Nylon 6,6 40 nm	1	2.0×10^2	0.035	0.99954
	2	3.3×10^2	0.045	0.99977
HDPE 30 nm	1	0.84	0.24	0.99323

Table 4. 2nd-order kinetics parameters determined by fitting kinetic-related data to Eq. (2) in n-butylacetate. r^2 is coefficient of determination.

Membrane	Test run	k / ppb$^{(1-n)}$*sec.$^{-1}$	C_E / ppb	r^2
Nylon 6,6 10 nm	1	37	0.020	0.99989
	2	1.6×10^2	0.020	0.99996
Nylon 6,6 40 nm	1	7.1×10^2	0.060	0.99657
	2	4.0×10^2	0.039	0.99459
HDPE 30 nm	1	67	0.12	0.98634
	2	19	0.13	0.95097

Table 5. 2nd-order kinetics parameters determined by fitting kinetic-related data to Eq. (2).in gamma butyrolactone. r^2 is coefficient of determination.

Membrane	Test run	k / ppb$^{(1-n)}$*sec.$^{-1}$	C_E / ppb	r^2
Nylon 6,6 10 nm	1	7.4	0.045	0.99996
	2	11	0.041	0.99955
Nylon 6,6 40 nm	1	$> 2.0\times10^3$	0.060	0.99984
	2	$> 2.0\times10^3$	0.057	0.99978
HDPE 30 nm	1	1.8×10^2	0.18	0.98498
	2	73	0.12	0.99626

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3.2 Equilibrium concentration (C_E)

Equilibrium concentration (C_E) is the Pd concentration in filter effluent at t=∞ and indicates removal efficiency at actual process condition, which is conventionally t = 5 to 20 s in point-of-use resist filtration. Figure 3 shows the averaged C_E and the averaged removal efficiency (1-C/C_0) of the various membranes in four different solvents. As a result, adsorption performance (1-C/C_0) of the all Nylon 6,6 filters at similar contact times was very efficient (0.9~ 0.95); however, C_E did not vary significantly with either membrane or solvent. Some variation with the solvent was found in HDPE 30 nm filter, but C_E values were, overall, greater than those for Nylon 6,6 filters (i.e., Nylon 6,6 filters demonstrated greater retention efficiency due to adsorption).

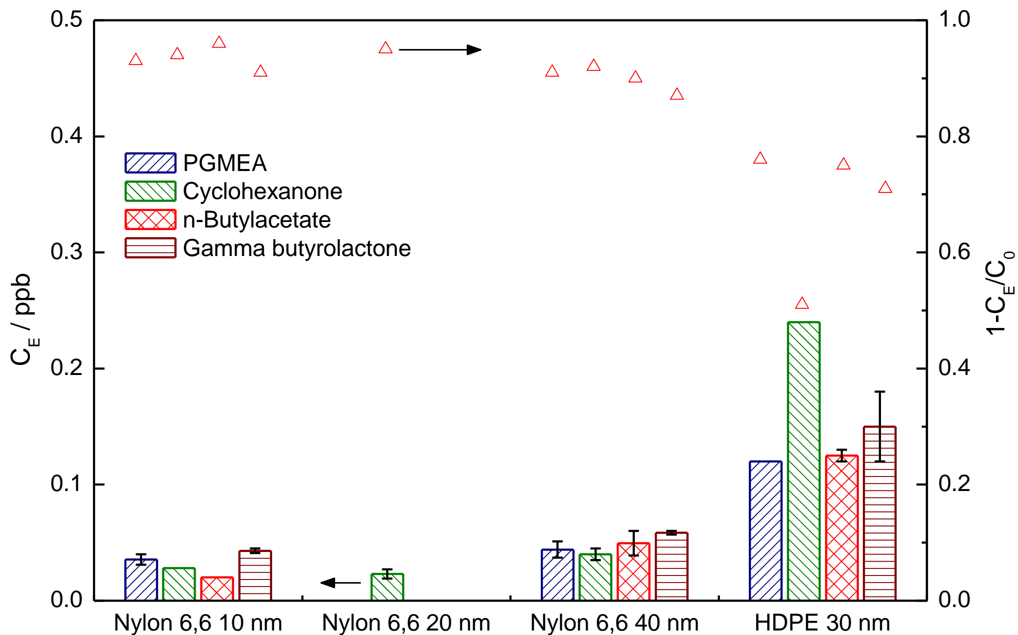

Figure 3. Average equilibrium concentrations (C_E, bars) and removal efficiency at equilibrium (1-C_E/C_0, triangles) of the Pd-Heptylamine on various filters in various lithography solvents. Error bars represent the ranges (max – min) of multiple test runs.

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3.3 Adsorption rate constant (k)

Adsorption rate constant (k) indicates the speed of adsorption and is determined by the slope of the kinetics curve during short contact times. The rise of the particle removal data was observed in only Nylon 6,6 40 nm and HDPE 30 nm and not observed in other filter membranes due to high inherent differential pressure (i.e., Contact time was not sufficiently minimized). In Figure 4, average k for Nylon 6,6 40 nm is compared to solvent properties that possibly affect k, such as octanol-water partition coefficient (Log P_{ow}), which indicates hydrophobicity (Greater values indicate increased hydrophobicity), and viscosity. Based on the results, k seems to depend on both solvent properties in Nylon 6,6 40 nm. In particular, k is greater in both lower-LogP_{ow} and lower-viscosity solvents.

A reason for k being greater in low viscosity solvent should be due to higher mobility of the nanoparticle in the low viscosity solvent. On the other hand, a possible reason for k being greater in hydrophilic (=low LogP_{ow}) solvent is that the current nanoparticle is stabilized with hydrophobic CH chain of the ligands, however, if the solvent is hydrophilic, the affinity of the ligand to the solvent is reduced and the interaction between the nanoparticle and the membrane is relatively enhanced. In the real resist, the above reasoning on the viscosity can be employed, however, the discussion on the solvent hydrophilicity should result in an adverse effect if the defect precursors are hydrophilic.

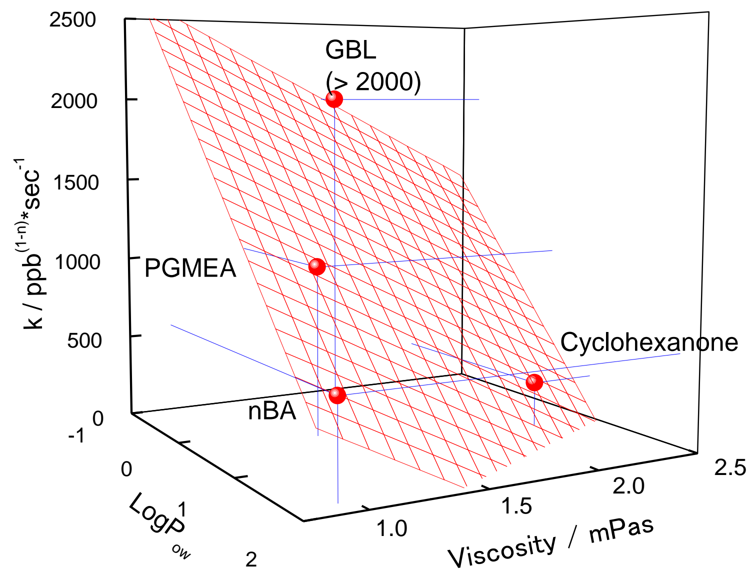

Figure 4. Adsorption rate constant (k) of Nylon 6,6 40 nm filter in Pd-HA challenge testing in various lithography solvents. Blue lines indicate coordinates projected on the xy-, xz-, and yz-planes. Red wireframe is a fitted plane of the k values.

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4. CONCLUSIONS

In conclusion, it is possible to predict that, in real lithography processes, adsorption removal performances of tested Nylon 6,6 membranes are similar among the various membrane grades and highly efficient within the solvent types tested. The adsorption rate in Nylon 6,6 40 nm filter was observed to be greater in both lower-LogP_{ow} (hydrophilic) and lower-viscosity solvents, possibly providing a direction for improved filtration performance based on the solvent properties. The complementary adsorption kinetics parameters give a more accurate suggestion for the filter performance in lithography applications combined with the conventional sieving filter ratings.

In real lithography processes, both adsorption and sieving should work as removal mechanisms. The results above suggested greater adsorption performance rating of Nylon 6,6 membrane materials than that of HDPE. Conversely, sieving performance can be rated using an established minimized adsorption protocol[7]. Combining these two ratings provides a filter that possesses both appropriate adsorptive performance and finer pore size, and eventually achieves more accurate suggestion for the filter performance in lithography application.

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