# Lithography

## Lithography Filtration: Enables Shrinking Device Geometries

Lithography is the key technology driver for the semiconductor industry. The industry's continued growth is a direct result of improved lithographic resolution. The complexity of today's fabricated semiconductor chips necessitates the use of numerous lithographic steps to achieve multilevel circuits.

Several key industry transitions have put an increased burden on contamination control in every aspect of the lithography process. These transitions include the implementation of DUV photoresist, adoption of top and bottom antireflective coatings, the trend towards thinner coatings and the use of immersion lithography. Each step introduces the possibility of deleterious particulate contamination, microbubble void defects and metallic contamination onto the wafer surface. The removal of particles that are smaller than the feature size is imperative to prevent circuit failure. Eliminating any air and preventing the formation of microbubbles is critical to reducing coating defects and increasing yields. Selecting the appropriate materials to minimize metallic contributions while optimizing dispense performance is essential for optimizing the coating process.

The use of bulk filters by photoresist manufacturers and point-of-use (POU) dispense filters by end users prevents the deposition of unwanted particles onto the wafer surface during the fabrication of the semiconductor chips.

The International Technology Roadmap for Semiconductors, published by the Semiconductor Industry Association, has cited the removal of particles 7 nm as critical for features at or smaller than 14 nm. The reduction of feature sizes to 7 nm or smaller has led to the offering of tighter membranes to insure the removal of yield reducing particles.

The method of delivering lithographic chemicals to the wafer surface is best accomplished by a precision dispense system. The point-of-use filter is an integral part of the dispense system, therefore careful selection of this filter is necessary to reduce defects on the wafer surface. In addition to particle and gel removal, minimization of microbubble formation, reduced chemical consumption and good compatibility are all key areas for point-of-use (POU) filter selection. Fortunately, several membrane materials are available for filtration of the variety of lithographic chemicals needed in the fabrication of today's and tomorrow's integrated circuits.

**Technical Issues in the Filtration of Lithographic Chemicals**

Several issues need to be considered when selecting a POU filter for your dispense system. These include the filter's particulate removal rating performance, hold-up volume to minimize photochemical waste, wettability of the filter membrane for efficient start-up, low operating and dispense pressure to prevent outgassing of photochemicals, and excellent compatibility to prevent particulate and metallic contamination. It is essential that the materials of construction are chosen for purity/cleanliness levels and are handled under non-contaminating conditions to prevent metal contamination.

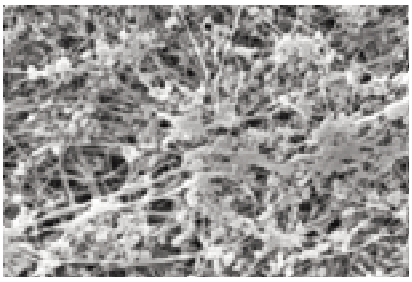
Optimized filter design reduces chemical usage during start-up and minimizes bubble formation that would cause defects on the wafer surface. Utilization of a large surface area and advanced filter membrane design yields low differential pressure, which maximizes gel removal efficiency and minimizes microbubble formation. Low operating pressure ensures that the filter will not cause photochemicals to outgas as it is dispensed from high pressure to low pressure. The prevention of metal contamination on the wafer surface necessitates careful material selection for the dispense system. Of course, compatibility of the chemical with all parts of the dispense system should always be assessed.

### Removal Efficiency

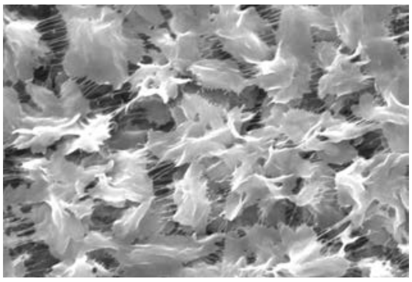
Removal of particles that could cause defects is accomplished by the appropriate selection of POU filters. The variety of microlithographic chemicals available necessitates the selection of the appropriate membrane material and micron rating to best accomplish the removal of particulate. Membranes are now available in PTFE (polytetrafluoroethylene), HDPE (high density polyethylene) and Nylon 6,6 (Figure 1), to meet particle removal and chemical compatibility requirements while providing instantaneous wetting of i-line and DUV photoresists, as well as anti-reflective coatings and developers. The surface tensions for some of the solvents used in microlithographic chemicals compared with the wettability of filter membranes are shown in Table 1. The table should be used as a guide, however most manufacturers add surfactants to their solutions, which would aid in the wetting of the filter membranes. The membranes for POU filtration are now available in micron ratings ranging from 1.0 µm to 10 nm.

The filtration of photosensitive chemicals such as photoresists, has shown no deleterious results on the performance of the chemical in an actual application. A study on the filtration[1] of actual photoresist showed no effects to the viscosity, coating thickness, molecular weight, or photospeed of the photoresist. The filters in the study were 0.1 and 0.05 micron rated Pall Falcon® filters with PTFE membrane.

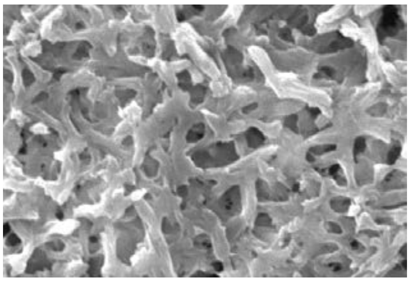
**Figure 1**



PTFE media shown at 5,000X magnification



High density polyethylene media shown at 5,000 X magnification

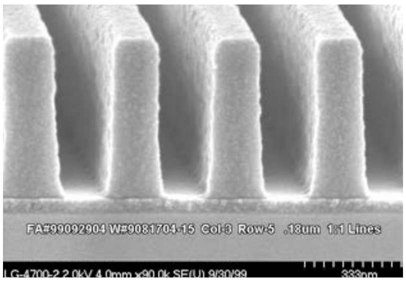


Nylon 6,6 media shown at 5,000 X magnification

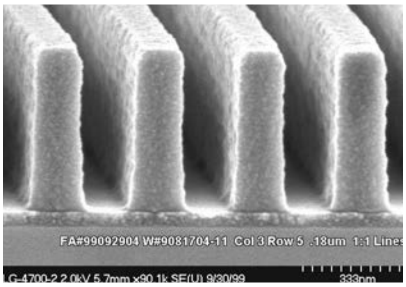
**Table 1**
**Surface Tension vs. Wettability of Filter Media**

| Solvent/Developer | Surface Tension (dynes/cm²) | Spontaneous Wettability | | |
|---|---|---|---|---|
| | | PTFE | Nylon 6,6 | HDPE |
| Acetone | 23 | Yes | Yes | Yes |
| Anisole | 35 | No | Yes | No |
| Butyl Acetate | 28 | Yes | Yes | Yes |
| Cyclohexanone | 35 | No | Yes | No |
| EGMEA | 32 | Yes | Yes | Yes |
| Ethyl Lactate | 29 | Yes | Yes | Yes |
| IPA | 22 | Yes | Yes | Yes |
| NMP | 41 | No | Yes | No |
| PGMEA | 28 | Yes | Yes | Yes |
| 2.5% TMAH/$H_2O$ | 70 | No | Yes | No |
| DI Water | 72 | No | Yes | No |
| Xylene | 28 | Yes | Yes | Yes |

## Figure 2




Top down SEM, 0.05 µm PTFE membrane




Top down SEM, 0.04 µm Nylon 6,6 membrane

In addition, a study[2] on 248 nm photoresist demonstrated that sub 0.1 µm filtration is possible for DUV photoresist. Filtration as fine as 0.03 µm utilizing two different types of dispense systems and 3 different media types did not alter the resist printing performance (Figure 2), thermal stability or process window (Figures 3 and 4). This demonstrates that particulate protection is possible as linewidths continue to shrink.

### Gel Removal

The removal of gels from photoresists depends greatly on the differential pressure across the dispense system. Point-of-use dispense filters should not contribute significantly to the differential pressure. In order to remove gels from photoresist and also prevent gels from extruding through the filter membrane onto the wafer surface, Pall has maximized the membrane surface area in the dispense filter. The high membrane surface area ensures both low inlet and differential pressure to maximize gel removal efficiency. The increased membrane area in the filter is accomplished by Pall's patented Ultipleat® design, which uses crescent shaped membrane pleats in the filter while retaining the overall footprint of the filter. The PhotoKleen™ EZD3 filters are designed to be used for most dispense pumps in the semiconductor industry.

### Ease in Venting (Minimal Microbubble Production)

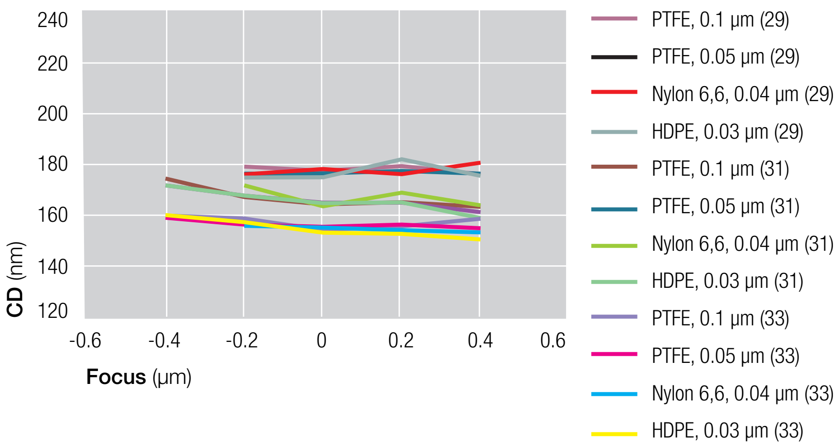
An additional source for defects on the wafer surface is from pinholes or microbubbles in the photoresist coating. These pinholes are due to trapped gas in the photoresist which can come out of solution as microbubbles. Microbubbles can be avoided if the filter design allows for easy venting during start-up and does not trap these bubbles for later release. The easy venting is accomplished by the PhotoKleen™ EZD3 pleated design that allows bubbles to move up the pleats and be released during the venting process. The design of Pall's point-of-use capsules also locates the vent and drain at the highest and lowest point of the capsule to ensure complete and easy venting and draining.

If the photoresist is exposed to a high differential pressure, dissolved gas will come out of solution and cause microbubbles to be released during dispense. A low differential pressure across the filter will prevent these gases from coming out of solution. Pall's Ultipleat filter design provides a low differential pressure across the filter and minimizes the release of bubbles during dispense.

### Low Operating Pressure

The push towards finer filtration has increased the operating pressure required to dispense photoresists. In addition, next generation, deep ultraviolet (DUV) resist materials are extremely sensitive to external environmental influences. The high surface area Ultipleat design provides a very low operating and differential pressure across the filter element (Figure 5). This minimizes outgassing of the photochemical and allows dispense at a much lower pressure. This may also minimize any potential damage caused by shearing of the complex photoresist polymers.

## Figure 3
## CD vs. Focus at mj noted - Cybor Pump



## Reduced Chemical Waste

The key to reduced consumption of photoresist is a small hold-up volume in the dispense system. A low hold-up volume filter design can reduce the start-up time because there is less volume of gas to vent. The rising prices of photochemicals, especially 248 nm and 193 nm DUV resists will make this a significant cost saving feature. The hold-up volume of the PhotoKleen™ EZD3 is less than 40 ml.

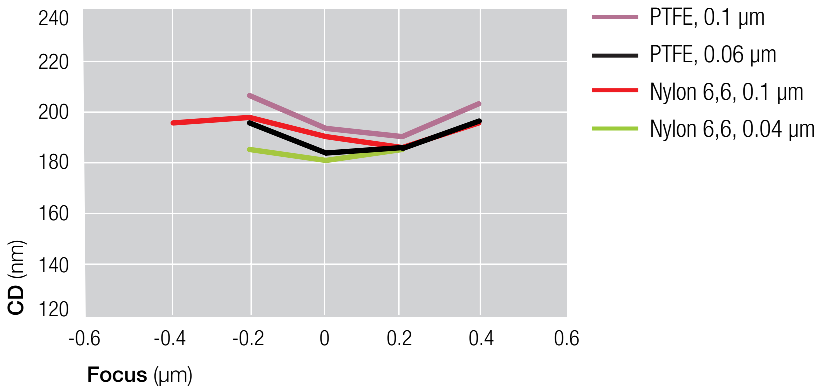
## Minimal Metal Contamination

The filter should contribute minimal contamination when used with solvents currently used in the microlithographic processes during IC fabrication. The International Technology Roadmap for Semiconductors published by the Semiconductor Industry Association has cited 5 ppb levels for ionic/metal contamination as the critical level for features at or smaller than 90 nm. Typical metal extraction levels for several dispense filters utilizing PTFE, HDPE and Nylon 6,6 with HDPE hardware and support material are shown in Table 2. In addition, an extensive extraction of P-Nylon Falcon filters was performed in 12 different base solvents (Table 2A).

## Conclusions

Several factors must be considered in the selection of the appropriate microlithographic filter. These factors include, the filter's particulate removal performance, hold-up volume, media wettability, operating and differential pressure, and material compatibility. Some of these factors may be more or less important depending upon the particular system or chemistry. The compatibility chart, wettability table and the Filter Recommendations (Table 3) should all be used to make the best filter selection. If you need additional assistance, please contact Pall Microelectronics, and we will be glad to provide you with a custom solution.

### Figure 4
### CD vs. Focus at 29 mj*

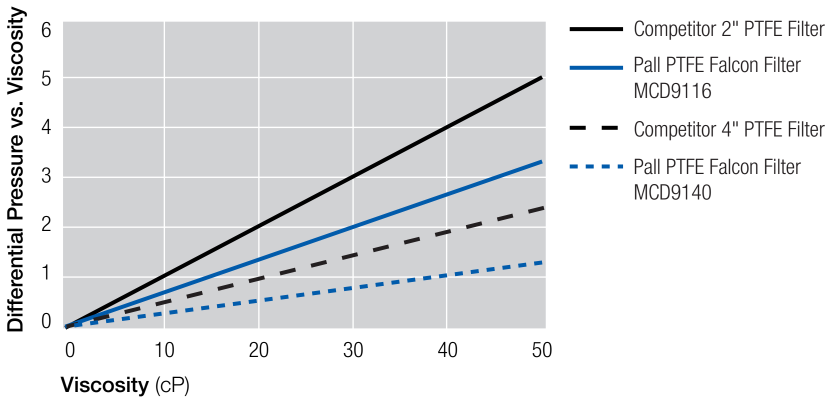



*CD as dispensed with IDI Model 450 pump

### CD vs. Focus at 31 mj*


*CD as dispensed with IDI Model 450 pump

### Figure 5
### Differential Pressure Versus Viscosity




**References:**

[1] Capitanio, Dennis; "Advantages to Point- of-Use Filtration of Photoresists in Reducing Contamination on the Wafer Surface", *ASMC98 Proceedings*, pp. 247-251, September 23-25, 1998

[2] Gotlinsky, Barry; "Measuring the effect of sub 0.1µm filtration on 248 nm photoresist performance" SPIE Microlithography Proceedings February 28-March 3, *Advances in Resist Technology 3999*, p. 138.

## Table 2 Solvent Soak Tests with Pall Falcon Filter

**The results of soaking Pall Falcon® filters (PTFE, Nylon 6,6 and HDPE Membranes) for 1 week static soa k in various solvents (500 ml). Analyses performed by ICP-AES. All levels are reported in ppb.**

| Element | Ag | Al | Ba | Ca | Cd | Cr | Cu | Fe | K | Li | Mg | Mn | Na | Ni | Pb | Sn | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ***Ethyl lactate*** | | | | | | | | | | | | | | | | | |
| HDPE | <1 | <1 | <1 | 2 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 20* | <2 | <2 | <2 | <1 |
| PTFE | <1 | 1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 21* | <2 | <2 | <2 | <1 |
| Nylon 6,6 | <1 | <1 | <1 | 2 | <1 | <1 | <1 | 1 | <2 | <1 | <1 | <1 | 25* | <2 | <2 | <2 | <1 |
| ***2-heptanone*** | | | | | | | | | | | | | | | | | |
| HDPE | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 4 | <2 | <2 | <2 | 2 |
| PTFE | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 3 | <2 | <2 | <2 | <1 |
| Nylon 6,6 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| ***Propylene glycol monomethyl ether acetate*** | | | | | | | | | | | | | | | | | |
| HDPE | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| PTFE | <1 | <1 | <1 | <1 | <1 | <1 | 1 | <1 | <2 | <1 | <1 | <1 | 3 | <2 | <2 | <2 | <1 |
| Nylon 6,6 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| ***N-butyl acetate*** | | | | | | | | | | | | | | | | | |
| HDPE | <1 | <1 | <1 | 1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 6 | <2 | <2 | <2 | 1 |
| PTFE | <1 | <1 | <1 | 1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | 5 | <2 | <2 | <2 | <1 |
| Nylon 6,6 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |

* Na in ethyl lactate could not be determined due to high baseline levels

## Table 2a Solvent Soak Tests with Pall P-Nylon Falcon Filter

**The results of soaking Pall P-Nylon Falcon® filters for 1 week static soak in various solvents (500 ml). Analyses performed by ICP-AES. All levels are reported in ppb.**

| Metals | Ag | Al | Ba | Ca | Cd | Cr | Cu | Fe | K | Li | Mg | Mn | Na | Ni | Pb | Sn | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-butyl acetate | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Ethyl cellosolve acetate | <1 | 1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Ethyl lactate | <1 | <1 | <1 | 2 | <1 | <1 | <1 | 1 | <2 | <1 | <1 | <1 | * | <2 | <2 | <2 | <1 |
| 2-heptanone | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Propylene glycol monomethyl ether acetate | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Methyl ethyl ketone | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| N,N-dimethyl formamide | <1 | <1 | <1 | <1 | <1 | <1 | 1 | ** | <2 | <1 | <1 | <1 | 3 | <2 | <2 | <2 | *** |
| N-methylpyrrolidone | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 2 | <2 | <1 | <1 | <1 | 3 | <2 | <2 | <2 | <1 |
| Ethyl 3-ethoxypropionate | <1 | <1 | <1 | 1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | **** | <2 | <2 | <2 | <1 |
| Methyl 3-methoxypropionate | <1 | <1 | <1 | 1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Ethyl pyruvate | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |
| Isopropyl alcohol | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <2 | <1 | <1 | <1 | <2 | <2 | <2 | <2 | <1 |

* Na in ethyl lactate could not be determined due to high baseline levels
** Fe in N,N-dimethyl formamide could not be determined due to high baseline levels
*** Zn in N,N-dimethyl formamide could not be determined due to high baseline levels
**** Na in ethyl 3-ethoxypropionate could not be determined due to high baseline levels

## Table 3
## Filtration Products Compatibility Guide

**R** Recommended for Use at Ambient Temperatures
**LR** Limited Recommendation
**NR** Not Recommended

Please contact Pall Microelectronics for specific recommendations.

| *Photoresist Solvents/ Developers* | Filter Cartridges | | | | | | Capsule Shell | | O-Rings | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ultipor® N66 | Ultipleat® P-Nylon | Emflon® | PTFE Falcon®/ P Emflon® | UltiKleen™ | PE-Kleen | Polypropylene | Polyethylene | EPR | FEP/Viton[1] | Kalrez[1] |
| Acetone | R | R | R | R | R | R | R | R | R | R | R |
| Aquatar | LR | LR | R | R | R | R | R | R | LR | R | R |
| Aquatar 2 | NR | NR | R | R | R | R | NR | R | LR | R | R |
| n-BA | R | R | R | R | R | R | R | R | R | R | R |
| Developer <3% TMAH | R | R | R | R | R | R | R | R | LR | R | R |
| Cyclohexanone | R | R | R | R | R | R | R | R | R | R | R |
| DMF | R* | R | R | R | R | R | R | R | NR | R | LR |
| EA | R | R | R | R | R | R | R | R | R | R | R |
| ECA | R | R | R | R | R | R | R | R | R | R | R |
| EEP | R | R | R | R | R | R | R | R | R | R | R |
| EGMEA | R | R | R | R | R | R | R | R | R | R | R |
| EL | R | R | R | R | R | R | R | R | R | R | R |
| EP | R | R | R | R | R | R | R | R | R | R | R |
| IPA | R | R | R | R | R | R | R | R | R | R | R |
| MAK | R | R | R | R | R | R | R | R | R | R | R |
| MEK | R | R | R | R | R | R | R | R | R | R | R |
| MMP | R | R | R | R | R | R | R | R | R | R | R |
| NMP | R | R | R | R | R | R | LR | LR | NR | R | LR |
| PGMEA | R | R | R | R | R | R | R | R | R | R | R |
| Xylene | NR | LR | NR | LR | R | LR | NR | LR | NR | R | R |

**Solvent Key**
**n-BA** n-butyl acetate
**ECA** Ethyl cellosolve acetate
**EL** Ethyl lactate
**MAK** 2-heptanone
**PGMEA** Propylene glycol monomethyl ether acetate
**MEK** Methyl ethyl ketone
**DMF** N,N-Dimethyl formamide
**NMP** N-Methylpyrrolidone
**EEP** Ethyl 3- ethoxypropionate
**MMP** Methyl 3-methoxypropionate
**EP** Ethyl pyruvate
**IPA** Isopropyl alcohol

* Recommended for filters with polypropylene hardware design.
[1] Viton and Kalrez are trademarks of E.I. du Pont de Nemours and Company