



## Metal Ion Removal from Photoresist Solvents - 1999 Microlithography Conference

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#### Abstract

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The trend toward narrower linewidths in the manufacture of integrated circuits has put an ever increasing burden on contamination control in every aspect of semiconductor fabrication. The number of microlithographic steps used in the fabrication of an integrated circuit has increased dramatically with the complexity of today's semiconductor chips. The removal of unwanted particle contamination from the photoresist before application to the wafer surface has been accomplished by filtration at the manufacturer of the photoresist as well as the end user. Metal ions in the photoresist now pose an ever increasing contamination problem with the feature sizes moving toward 0.25 micron and smaller. The removal of unwanted metal ions from the photoresist prior to application of the photoresist to the wafer surface will reduce device defects due to metal contamination.

The introduction of a metal ion removal device to reduce the final metal ion content of photoresists will drastically reduce the exposure of the wafer surface to these contaminants. The reduction of metal ion concentration from several hundred ppb to single digit ppb will be demonstrated in single pass application of this device. Utilization of this technology will reduce the incidence of defects during the fabrication of the integrated circuit.

**Keywords:** photoresist, metal, contamination, defect, solvents, semiconductor, filtration, ion

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#### 1. Introduction

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Fabrication of semiconductor devices requires pattern definition through microlithographic processes. These processes are some of the most critical and sensitive processes used in semiconductor fabrication. As feature sizes decrease and the number of devices increase, the resulting device complexity has resulted in the need for lower levels of contamination.

The trend in the industry is toward smaller features of 0.25 micron and smaller. The complexity of the fabricated semiconductor chips necessitates the use of numerous microlithographic steps to achieve the several layers circuits in these compact chips. Each microlithographic step introduces the possibility of deleterious contamination onto the wafer surface. The removal of particulate contamination has been addressed with point of use filtration. However, metal ion contamination introduced by the photoresist can also lead to failure in the integrated circuit. Not only can metal ion contamination have a potential impact on the present layer being fabricated but ashing of the photoresist may cause a mobile specie to diffuse into the lower layers and impact integrity and limit yield. The reduction of these metal contaminants in the solvents used to manufacture these photoresists will reduce the exposure of the wafer to these types of contaminants.

For the rapid removal of these metal ion contaminants, a chemically modified polyethylene porous membrane has been developed to serve as filter and purifier. Ion exchange groups are incorporated into the media and remove the metal contaminants rapidly without the long residence time needed for standard methods. The filter was developed to remove metal ion contaminants from organic solvents or mixed solvents, which are materials used for photoresist manufacture. The filter is the first

commercialized product in the market specifically designed for the organic solvent application. This study was undertaken to demonstrate the filter membrane's capability of reducing metal ion contamination from several common photoresist solvents.

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## 2. Experimental Procedures

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### 2.1 Experimental test stand

For this study filter capsules were used to demonstrate removal efficiency of the metal ion removal filter in a small scale environment. The capsules contained 47 mm diameter discs of the membrane with PFA supports and shell. The solvents used in this study were pumped from a HDPE (High Density Polyethylene) reservoir through PTFE (Polytetrafluoroethylene) tubing into the filter capsule. A schematic of the test stand is shown in Figure 1.

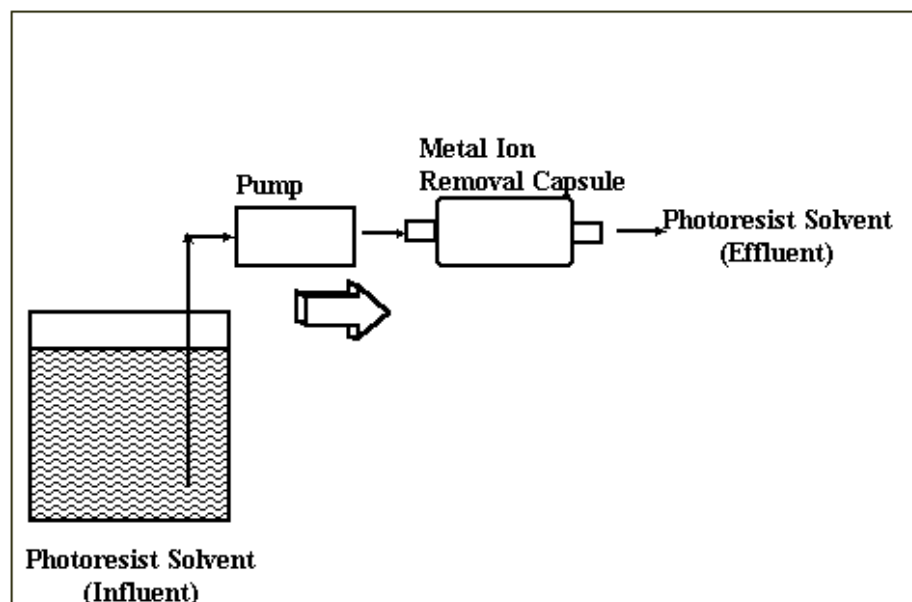
Figure 1: The schematic of the test stand used in the evaluation of the capsules for metal ion removal of photoresist solvents

### 2.2 Experimental procedure

Prior to the introduction of the solvents into the test stand, the reservoir, pump and tubing were flushed with clean solvent to insure that the equipment would not contaminate the testing. The flushing solvent was tested by a Hewlett Packard Model 4500 ICP-MS (Inductively Coupled Plasma – Mass Spectroscopy) to insure no additional impurities were added by these parts of the test stand. The test solvent was then loaded into the reservoir and pumped through the tubing and into the test capsule. The effluent was then analyzed by ICP-MS and compared with the influent to determine the capsule's ability to remove metal ion contamination from the solvents. In some cases the influent solvent was "spiked" to increase the challenge level to the capsules. Typical flows through the capsule were 4 mL/min. Testing on ethyl lactate (EL), ethyl 3-ethoxy propionate (EEP), propylene glycol monomethyl ether acetate (PGMEA) and 2-heptanone (MAK) was undertaken to demonstrate the device's efficiency.

### 2.3 Membrane capacity testing

A sample of ethyl lactate (EL) was strongly spiked to demonstrate the removal capacity of the filter capsule under these testing conditions. Levels of sodium (Na) and iron (Fe) were added at 2.61 and 1.9 ppm, respectively. Samples of effluent were collected as a function of time and analyzed for Na and Fe by ICP-MS. The effluent levels were monitored until breakthrough of the Na and Fe was observed. The breakthrough point was defined as the point at which the effluent exhibits increasing levels of the metal ion contaminants.



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## 3. Experimental Results

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### 3.1 Metal ion removal results

The results of testing on ethyl lactate (EL), propylene glycol monomethyl ether acetate (PGMEA), ethyl 3-ethoxy propionate (EEP), and 2-heptanone (MAK) are shown in Table 1. The results are actual levels of contaminants in the solvent except for the ethyl lactate that was spiked to increase levels of contamination to show the device's removal efficiency. The results demonstrate a removal efficiency of > 95% for total

metal ion contamination and the results are especially demonstrated on Na, Fe, chromium (Cr) and zinc (Zn) metal ion contaminants.

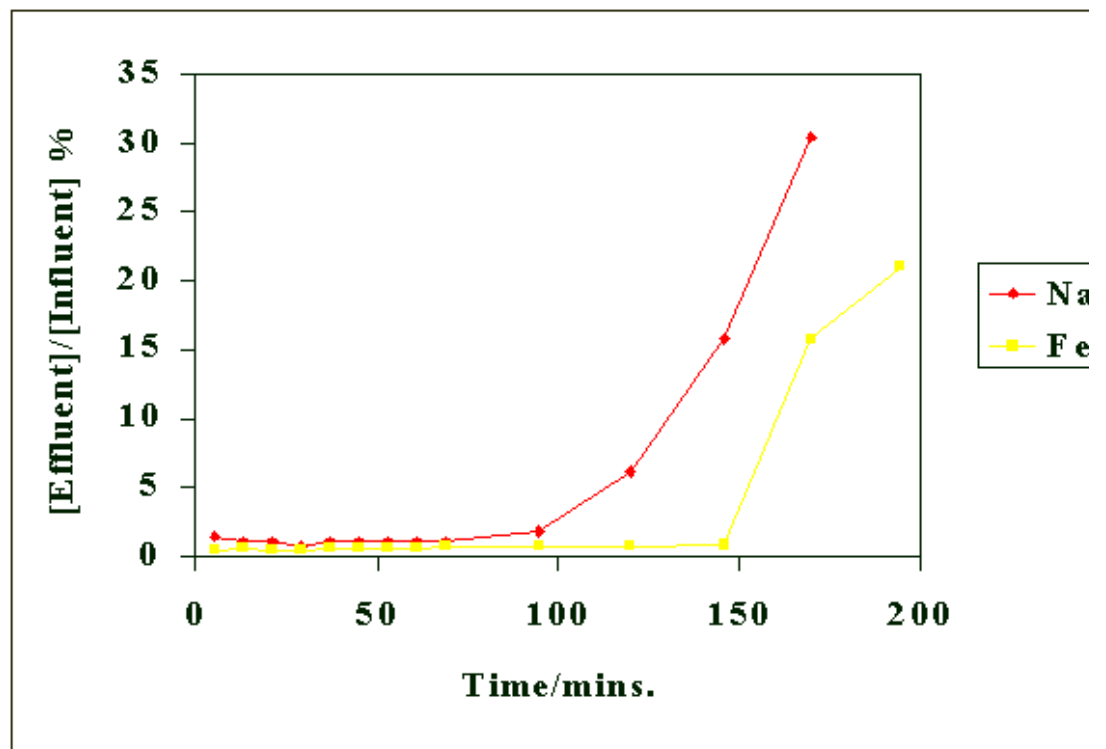
Table 1: The metal ion contaminant levels in the solvent before and after treatment with the filter capsule

Metal Ion	Det. Limit ppb	MAK ppb		EEP ppb		PGMEA ppb		EL ppb (Na,Fe added)		EL ppb (Na,Fe,Cr added)	
		Before	After	Before	After	Before	After	Before	After	Before	After
<b>Al</b>	0.1	3.4	0.5	<DL	<DL	0.9	<DL	<DL	<DL	<DL	<DL
<b>B</b>	2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>Ca</b>	3	64	8.1	<DL	<DL	3.5	<DL	<DL	<DL	<DL	<DL
<b>Cr</b>	0.5	2.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	228	<DL
<b>Cu</b>	0.5	11	0.8	<DL	<DL	6.8	<DL	<DL	<DL	<DL	<DL
<b>Fe</b>	2	20	<DL	<DL	<DL	12	<DL	2100	33	85	<DL
<b>Pb</b>	0.1	6.5	<DL	<DL	<DL	2.9	<DL	<DL	<DL	<DL	<DL
<b>Li</b>	0.05	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>Mg</b>	0.1	9.7	1.1	1	0.8	0.6	<DL	<DL	<DL	<DL	<DL
<b>Mn</b>	0.1	0.6	<DL	<DL	<DL	0.2	<DL	<DL	<DL	<DL	<DL
<b>Ni</b>	0.1	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>K</b>	3	<DL	3.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>Na</b>	0.1	860	4.3	64	3.6	310	0.6	2200	5.8	130	<DL
<b>Sn</b>	1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>Ti</b>	1	2.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
<b>Zn</b>	0.5	150	0.9	4.7	<DL	690	<DL	1.3	<DL	1.3	<DL

### 3.2 Capacity testing results

The challenge of high levels of metal ion contaminants on the filter capsule was measured by the efficiency of removal of Na and Fe as a function of time. The levels of challenge in this case were much higher than expected in photoresist solvents but were undertaken to show capacity of the filter membrane and the gradual breakthrough of contaminants after capacity has been reached. The sites on the membrane eventually become occupied and reduced efficiency was observed at the breakthrough. The breakthrough is fairly sharp yielding high removal efficiency to the point of breakthrough. The profile for the 2.61 ppm and 1.9 ppm simultaneous challenge are shown in Figure 2. The results have indicated a 1 milligram capacity for removal for the membrane area in the filter capsule. This will allow users to estimate the filter usage to remove metal contamination in their solvents to achieve overall specifications for their products.

Figure 2: Profile of the retention of the metal ion removal filter with simultaneous challenge of 2.61ppm of sodium and 1.9 ppm of iron.



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## Conclusions

The specially developed polyethylene membrane incorporating ion exchange groups has been shown to reduce metal ion levels from several hundred ppb to single digit ppb in single pass operation. Contamination of ~ 2 ppm was reduced to double digit ppb also in single pass operation.

The National Technology Roadmap for Semiconductors (1997) published by the Semiconductor Industry Association has sighted 5 ppb levels for ionic/metal contamination as the critical level for features at or smaller than 0.25 micron. This technology will enable reduction of ionic/metal contamination on the surface of the wafer during fabrication of 0.25 micron and finer features via purification of the photoresist solvents.

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