Separation and Purification Sciences Division

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3M Immobilized Micro-Bed Ion Exchange Resin Bed Technology Treatment of PGMEA

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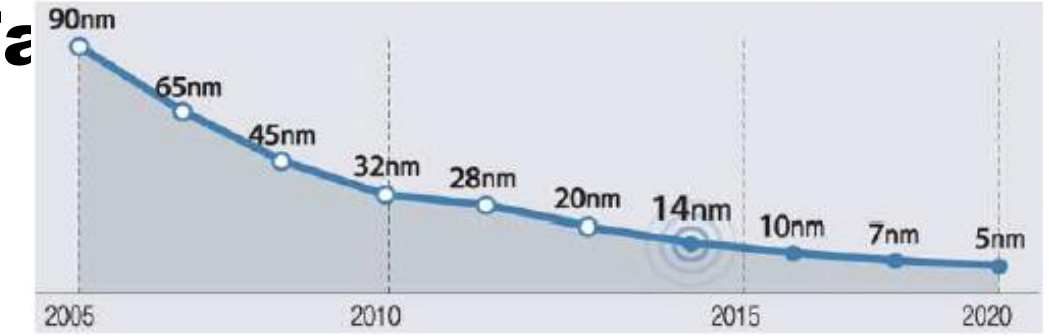
Next Generation, Finer, Cleaner, Fa



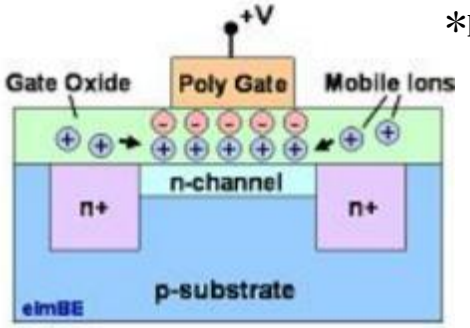
- The continued trend to smaller feature size, thinner layers, 3D architecture require tighter contamination control.
- Metal ions are mobile and can diffuse in or out of the active components, resulting in either reduction in yield, reliability, and/or performance of the circuits.
- All the metals will be the threats to advanced nodes.
- The challenge today is to reduce the metal

Patterns	>14Nano	<10Nano	<7Nano	<5Nano	<3Nano
Metal Ion removal	<1ppb	<0.05ppb (<50ppt)	<0.01ppb (<10ppt)	<0.01ppb (<10ppt)	<0.50bbp 500 ppq
Target Metal Ion	23-27	All	All	All	All
Particle counts	0.04um, <300 pcs/ml	0.03um, <50 pcs/ml	0.02um, <10 pcs/ml	0.02um, <10 pcs/ml	0.02um, <10 pcs/ml

*Resource: IRDS

YEAR OF PRODUCTION	2015	2017	2019	2021	2024	2027	2030
Logic device technology naming	P70M56	P48M36	P42M24	P32M20	P24M12G1	P24M12G2	P24M12G3
Logic industry "Node Range" Labeling (nm)	"16/14"	"11/10"	"8/7"	"6/5"	"4/3"	"3/2.5"	"2/1.5"
Logic device structure options	finFET FDSOI	finFET FDSOI	finFET LGAA	finFET LGAA VGAA	VGAA, M3D	VGAA, M3D	VGAA, M3D

2015 ITRS 2.0 More Moore, fig. 3, pg. 18



Mobile Ionic Contaminants in gate oxide**

**Figure resource from www.eesimi.com

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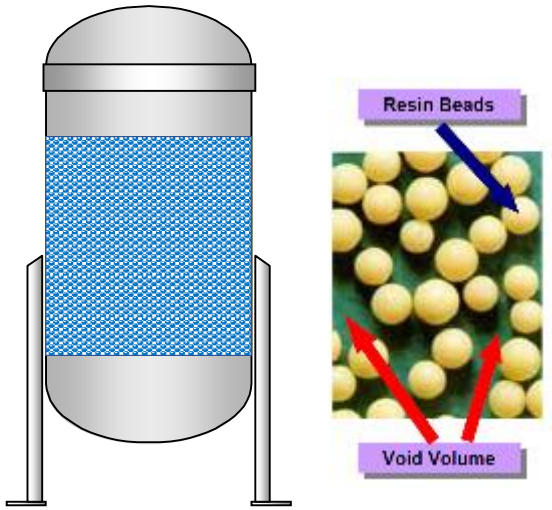
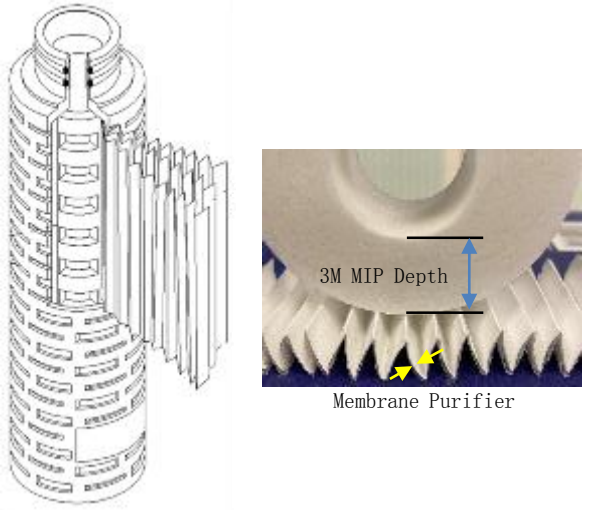
Strategies for removing metals

Ion Exchange columns



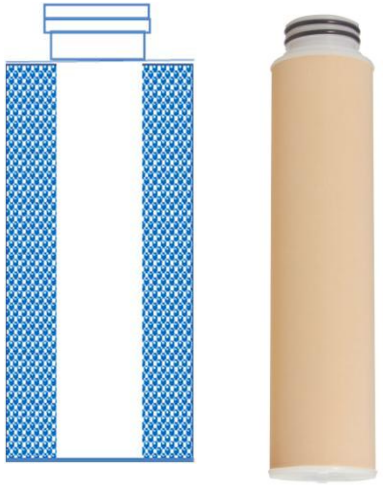
High Capacity
Thick bed depth
Potential for channeling
Low utilization

Ion Exchange Membranes



Thin layer
Limited Capacity vs beds
Low residence time,
Incorporating a membrane

3M Metal Ion Purifier



Uniform, fix-bed structure,
High Capacity,
Tortuous Path,
High residence time

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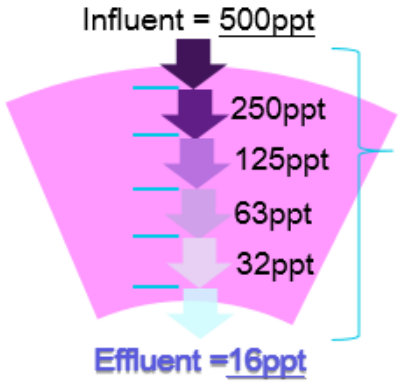
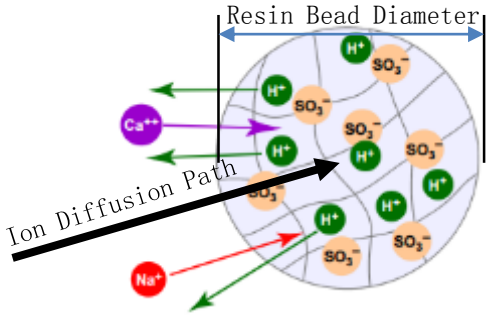
3M Metal Ion Purifier Introduction

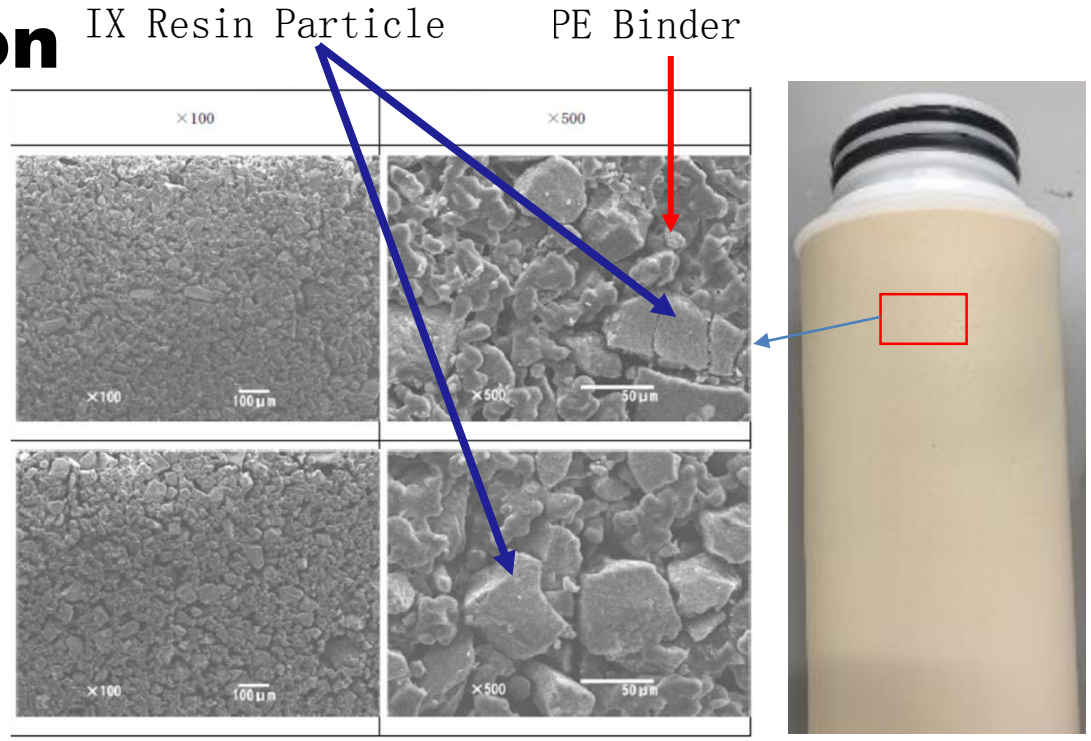
- Immobilized Micro-Bed Ion Exchange Resin Technology
  - ✓ IX Resin immobilized in PE matrix to form depth monolith structure with long tortuous porous path;
- Feature and benefit:
  - ✓ High internal surface area for metals to be removed;
  - ✓ Higher residence time;
  - ✓ Shorter ion diffusion path due to smaller resin diameter;
  - ✓ Higher ion exchange capacity, higher throughput;
  - ✓ Uniform porosity and submicron pore prevent channeling of the chemistry;
  - ✓ Minimize metal and particle extractable ;
  - ✓ High efficient reduction of metal ion to PPT level;



Monolith model to remove metal



Ion Diffusion Radius*



SEM Photo of 3M Metal Ion Purifier

Data sheet of 3M Metal Ion Purifier		
10" Cartridge	SCP	APP
Ion Exchange	Strong Acid Cation Exchange (H-form)	Chelating Resin Amino Phosphate
Binder Resin	Ultrahigh Molecular Weight Polyethylene (UHMWPE)	
Typical Ion Exchange Capacity (90% efficiency)	450mEq/10"	460mEq/10"
End Caps	High Density Polyethylene (HDPE)	
O-Ring	Perfluoroelastomer (FFKM)	

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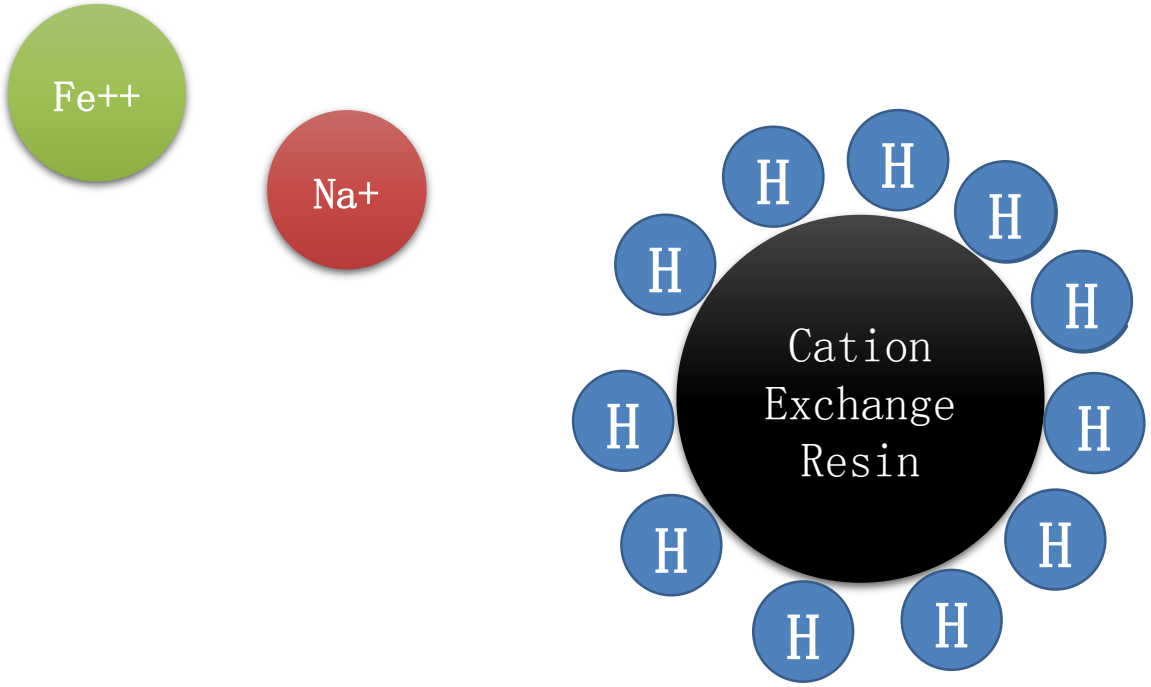
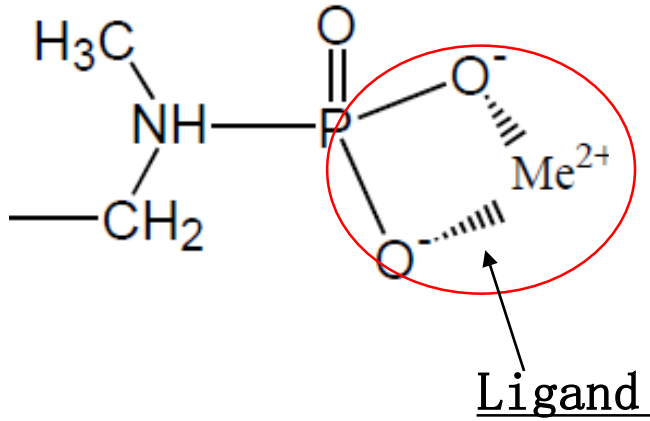
Chemistry of SCP and APP Metal Ion Purifier



$Cu^{++} > Pb^{++} > Fe^{++} > Mn^{++} > Ca^{++} > Mg^{++} > Na^{+} > H^{+}$

Ion Exchange by Strong Acid Cation Exchange Resin



Metal Chelation by Amino Phosphate

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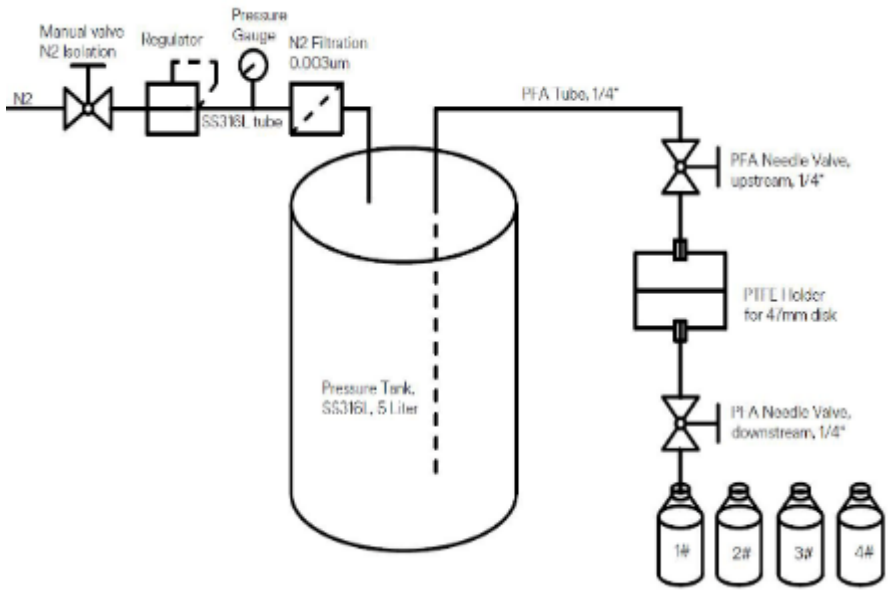
Experimental

- Test Liquid:
  - ✓ PGMEA is the key solvent for photoresist and lithography;
  - ✓ Raw PGMEA is SEMI Grade 2;
- Test Material
  - ✓ 47mm Metal Ion Purifier with 3mm thickness;
  - ✓ Two types of resin: SCP and APP Chemistry;
- Test System and Operation
  - ✓ Constant Pressure Test by High Purity Nitrogen;
  - ✓ Operating Pressure 20-50kpa;
  - ✓ Flow rate: 20-40ml/min;
  - ✓ Test instrument: ICP-MS(20 metals), #1-5 samples;
  - ✓ Pre-treatment to 47mm discs

47mm discs of 3M Metal Ion Purifier

47mm discs PTFE Holder



Schematic layout of the test system

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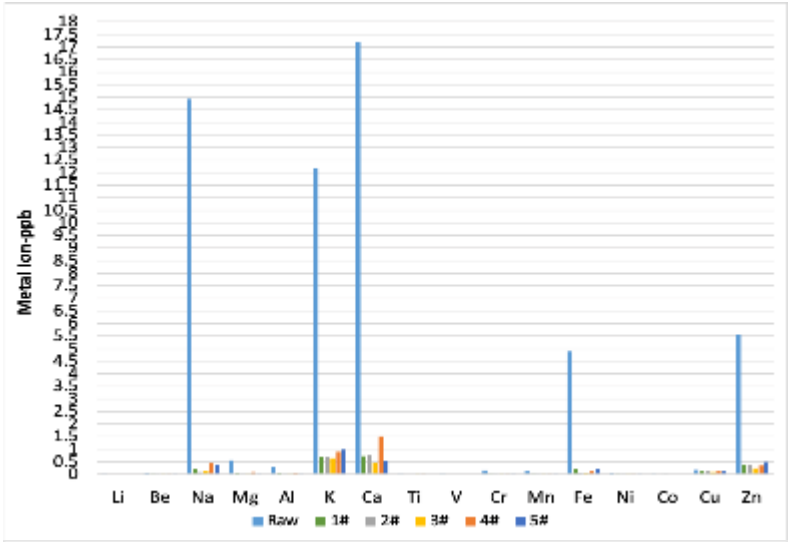
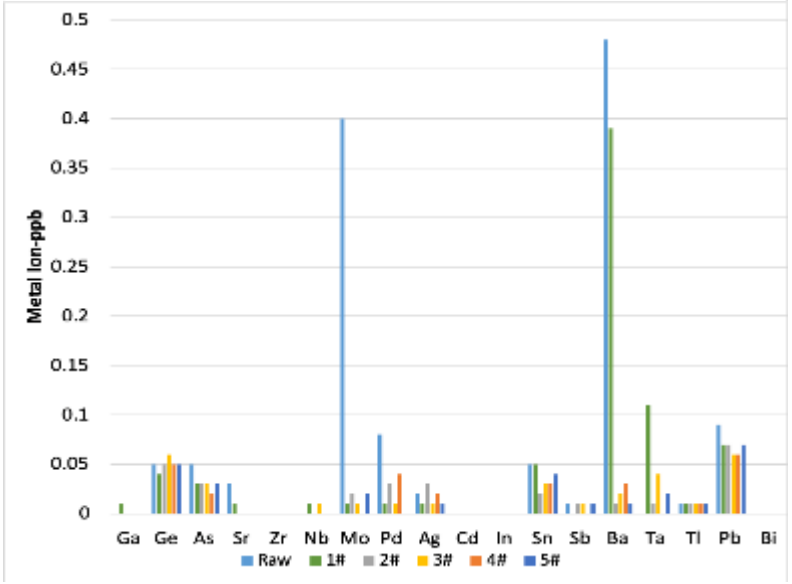
Test Results of SCP Metal Ion Purifier in PGMEA

- All of metal contents were reduced to below 1 ppb, no matter how much higher starting concentrations;
- The main target metals, Na, Ca, Mg, Al, Fe, and Zn, are reduced significantly to below 0.5ppb, K is reduced to 0.98ppb from 12.18ppb;
- Many of the metal ion removal efficiency is higher to above 90%, irrespective of starting concentration;
- SCP is made of strong acid cation IX resin, which is beneficial to remove ionic metals, such as alkali metals and alkali-earth metals.
- The metal ion concentration in the outlet is kept consistent with low variation;





Metal Ion Abbrev.	Concentration of samples-ppb		
	Influent	*Effluent at 2L*	*Efficiency at 2L*
Li	0.01	0	100.0%
Be	0.05	0.02	60.0%
Na	14.93	0.37	97.5%
Mg	0.57	0.03	94.7%
Al	0.3	0.04	86.7%
K	12.18	0.98	92.7%
Ca	17.18	0.50	97.0%
Ti	0.01	0	100.0%
V	0.01	0	100.0%
Cr	0.16	0.01	93.8%
Mn	0.11	0.04	63.6%
Fe	4.9	0.19	96.1%
Ni	0.08	0.01	87.5%
Co	0.01	0	100.0%
Cu	0.18	0.12	33.3%
Zn	5.54	0.49	91.2%
Ga	0	0	
Ge	0.05	0.05	
As	0.05	0.03	40.0%
Sr	0.03	0	100.0%
Zr	0	0	
Nb	0	0	
Mo	0.4	0.02	95.0%
Pd	0.08	0	100.0%
Ag	0.02	0.01	50.0%
Cd	0	0	NA
In	0	0	NA
Sn	0.05	0.04	20.0%
Sb	0.01	0.01	0
Ba	0.48	0.01	97.9%
Ta	0	0.02	0
Tl	0.01	0.01	0
Pb	0.09	0.07	22.2%
Bi	0	0	NA

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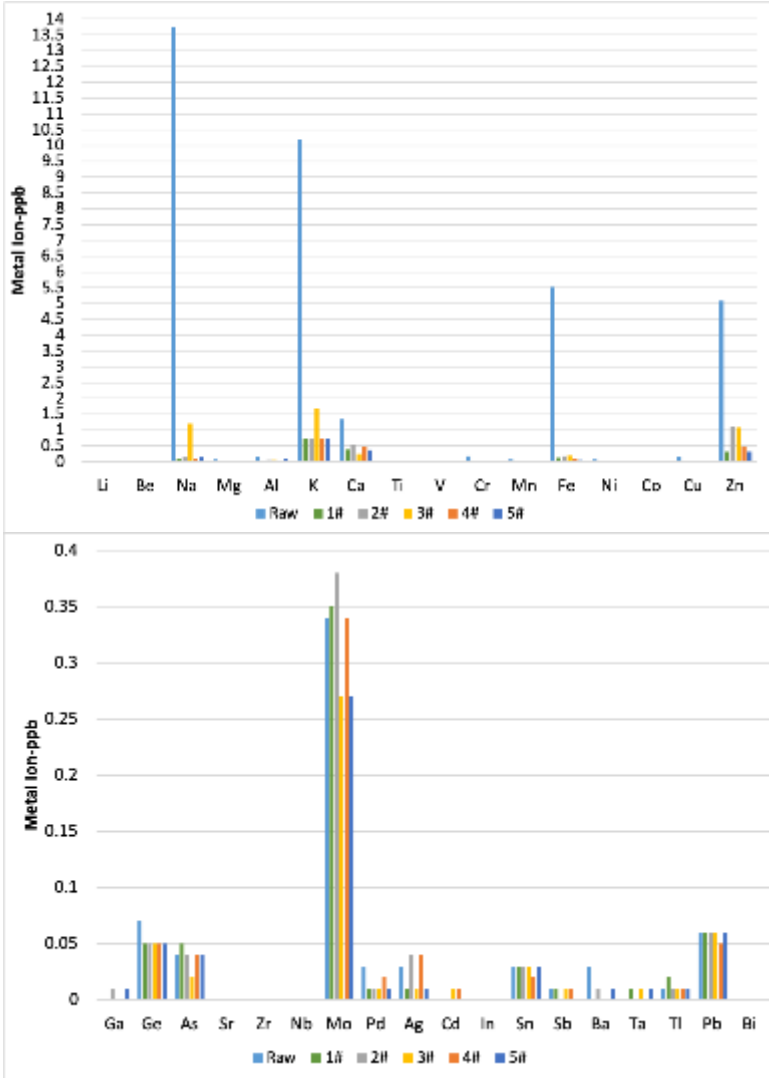
Test Results of APP Metal Ion Purifier in PGMEA

- APP demonstrate a similar trend of metal ion reduction with SCP. All the metals are reduced to below 1ppb.
- The main target metals, Na, Ca, Fe, and Zn, are reduced significantly to below 0.5ppb, K is reduced to 0.73ppb from 10.2ppb;
- APP showed higher capability to remove heavier metals, such as Fe, Ni, Co, Cu, and Zn;
- Iron removal efficiency is as high as 99.1%, and Cu removal efficiency is 93.8% even with starting concentration at 0.16ppb;



Metals-Abbrev.	Concentration of samples-ppb		
	Influent	*Effluent at 2L*	*Efficiency at 2L*
Li	0	0	NA
Be	0.01	0.01	0
Na	13.75	0.14	99.0%
Mg	0.07	0.02	71.4%
Al	0.16	0.09	43.8%
K	10.2	0.73	92.8%
Ca	1.34	0.36	73.1%
Ti	0.01	0.01	0
V	0.01	0	100.0%
Cr	0.18	0.03	83.3%
Mn	0.08	0.02	75.0%
Fe	5.52	0.05	99.1%
Ni	0.08	0.01	87.5%
Co	0.01	0	100.0%
Cu	0.16	0.01	93.8%
Zn	5.08	0.31	93.9%
Ga	0	0.01	NA
Ge	0.07	0.05	28.6%
As	0.04	0.04	0
Sr	0	0	NA
Zr	0	0	NA
Nb	0	0	NA
Mo	0.34	0.27	20.6%
Pd	0.03	0.01	66.7%
Ag	0.03	0.01	66.7%
Cd	0	0	NA
In	0	0	NA
Sn	0.03	0.03	0
Sb	0.01	0	100.0%
Ba	0.03	0.01	66.7%
Ta	0	0.01	NA
Tl	0.01	0.01	0
Pb	0.06	0.06	0
Bi	0	0	NA

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Conclusion

- 3M Metal Ion Purifier based on immobilized monolith ion exchange resin technology can reduce metal contaminants from PGMEA to PPT level with high efficiency;
- Utilize a single pass, the metal concentration in the outlet of Metal Ion Purifier can be reduced to low PPT, potentially to PPQ level ;
- 3M Metal Ion Purifiers can be widely used to remove metal ions from many high purity solvents, resins, monomer, polymer and other lithography chemistries, such as SOC, BARC, etc;

Photoresist Composition (Typical Example)

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