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Next generation purification method for achieving low trace metals in ultra-high purity chemicals

Majid Entezarian[a], Mitsuaki Kobayashi[b], Yukihisa Okada[b], Takaaki Shirai[b], Keita Abe[c], Taiji Yamasaki[c], Robert Gieger[a]
[a] 3M Separation and Purification Sciences Division, 400 Research Parkway, Meriden CT, USA 06450;
[b] 3M Separation and Purification Sciences Division, and [c] 3M CRSL
3-8-8 Minami Hashimoto, Chuo-ku, Sagamihara-shi, Kanagawa 252-5285

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Proc. SPIE 11612, Advances in Patterning Materials and Processes XXXVIII, 116120S (22 February 2021); https://doi.org/10.1117/12.2583882

***Abstract*—The high purity requirements of materials used in semiconductor manufacturing are being pushed to unprecedented levels as demand for reliability in computer processors over increasingly longer lifetimes continues to rise. The production of these high purity chemicals requires new purification methods and technologies. One of the limiting factors in purification process is to bring the metal impurities into close contact with purifying surfaces. Current metal reduction techniques rely on ion exchange technology however, the pathways are large in comparison with the size of the unwanted metal species. A new approach is required to increase the probability of contact between the metal species with the exchange surface. In addition, fluid channels need to be mixed, rotated, and inverted in order to increase the probability of surface contact.**

The new approach discussed in this paper would present a method for dividing the fluid through micro-channels that form tortuous pathways. These micro-channels allow for further dividing and converging of the fluid thereby presenting the metal species to the purifying surfaces throughout the porous matrix.

Several high purity chemicals such as PGMEA used in microelectronic industries were purified using the above approach. The metal concentrations of low parts per billion (ppb) were effectively reduced to low parts per trillion (ppt). The ion exchange capability was a function of the concentration and the presence of the species in the solution. Two ion exchange chemistries of strong acid and chelating were made into these structures and their purification performances were assessed and compared in terms of removal efficiencies. Furthermore, these two chemistries were evaluated in series to demonstrate the overall synergistic purification capabilities.

***Keywords*—High Purity Chemicals, Metal Reduction, Ion Exchange, Advanced Photolithography**

1. Introduction

As the number of transistors are increasing in electronic devices, the feature sizes are decreasing to levels that impurities play a critical role in the manufacturing, function, and longevity of advanced devices. These impurities are usually classified as cations usually in the form of metal ions, anions of chlorine or hydroxide, or as organic compounds in the form of low to high molecular weight. The removal of these impurities from any fluid that comes in contact with these devices during the manufacturing process is paramount to improving yields and enabling these devices that will shape the future technological advances in medical, diagnostics, communications, artificial intelligence and many more.

The fluids that are coming in contact with a wafer during its manufactures are Ultra-Pure Water (UPW), etchants, cleaning solutions, Photoresists, developers, coatings, and Chemical Mechanical Planarization (CMP) slurries.

There are several purification methods that can be used for purifying fluids. These are evaporation and distillation, affinity purification, filtration, adsorption, fractionation, electrolysis, and ion exchange to just name a few. The focus of this study was the use of ion exchange mechanism. It is stated that the ion exchange process is a controlled solely by the diffusion, which is dictated by the materials micro- and macro-structures[1].

1. Introduction - continued

One approach that has been utilized to overcome some of the diffusion challenges is to reduce the pore size by utilizing a membrane and grafting an ion exchange on to the membrane surface[2]. Providing high ion exchange capacity does not always results in higher purification outcome. This is more pronounced when approaching very low concentrations for the start. When approaching low ppb metals level and the objective is to achieve low ppt, the diffusion is becoming the rate limiting factor. There are several parameters that can be applied to increase diffusion such as (a) temperature and (b) concentration increases. These effective changes are not possible for high purity and advanced photo chemistries. Another approach to improve diffusion is reducing the (c) diffusion path. This is achieved by flowing the fluid through narrower channels. Assuming the ionic species are the center of the channel, which would be the farthest from the channel walls, the reduction of the channel width directly reduces the diffusion path and reducing the diffusion time. Another approach is to (d) increase the surface contact area between the fluid and the active ion exchange surface, or residence time. Using smaller pore sizes, increasing number of pores, and lengthening of the porous structure would result in increased contact between the fluid and the active surface. Furthermore, dividing the fluid to numerous channels and converging and diverging the stream (e) increases mixing the likelihood of the species coming in contact with active surfaces. The 3M Metal Ion Purifiers are building on the above diffusion-controlled parameters by presenting the ion exchange in an immobilized porous micro-channel microstructure. This structure is a porous tubular format, with a similar industry form factor to filtration cartridges. The interaction of the fluid and the microporous immobilized structure is of great interest.

2. Methodology

Surface Area Measurements

The samples were placed in 9 mm tubes. Outgassing was performed at 60 °C for 14 hours prior to analysis under <20 mTorr of pressure. The samples were analyzed at liquid nitrogen temperature (~77 K) using ultra high purity nitrogen gas. Void volume was determined using helium. 16 points were taken (adsorption branch) from 0.01 P/Po to 0.3 P/Po. The points between 0.05 P/Po and 0.3 P/Po were fit to the BET equation. The instrument used for this analysis was a Quantachrome (Anton-Parr) Autosorb IQ2-MP.

Metal Analysis

All samples were analyzed using Agilent 8900 ICP-QQQ instruments. System was acid washed several times to obtain a below detection samples before running the tests. Controls were incorporated into the test plan to ensure the elimination of extraneous factors. The sample aliquots were collected by volume intervals processed through the ion exchange blocks.

Raw Materials

In this study, two types of 3M immobilized ion exchange resin products were evaluated. One type is composed of strong acid cation exchange chemistry, identified as “SCP”. The other type is based on an amino phosphate chelating chemistry and is identified as “APP”.

Computation Fluid Dynamics (CFD)

The ANSYS Fluent Release 16.0 was used for all the CFD work

Ion Exchange Challenge Experiments

The test set-up is shown in Figure 1. The PGMEA was transferred into a 1L pressure tank and pushed through the system by increasing the pressure of the pressure tank. High purity nitrogen gas was used to pressurized and maintain a constant pressure. The test pressure was adjusted by a compressed gas regulator. Nitrogen was filtered to 0.003 µm rating to ensure no particulate was introduced into the fluid through the nitrogen line. Prior to starting the test, the 47 mm disc was installed into the high purity PTFE holder and sealed to prevent any bypass or leaks. Downstream of the housing, a needle valve was installed for adjusting the flow rate. The discs were soaked in the solution for a period of 24 hours to ensure the structure is fully wetted by the fluid and the air in the pores is replaced with the fluid in order to maximize the utilization of the ion exchange capacity. After completion of the soaking period, the initial 100 ml sample was discarded, and subsequent filtrate was collected in high purity 250 ml PFA bottles. The untreated sample was labeled as “Raw” and the subsequent samples were labeled 1 through 5. All the samples were sealed immediately after filling and opened only when ready for metal analysis using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). More than twenty metal elements were analyzed to assess the effectiveness of each ion exchange chemistry. The samples were analyzed as a function of processed volume through each ion exchange and the removal efficiency were calculated.

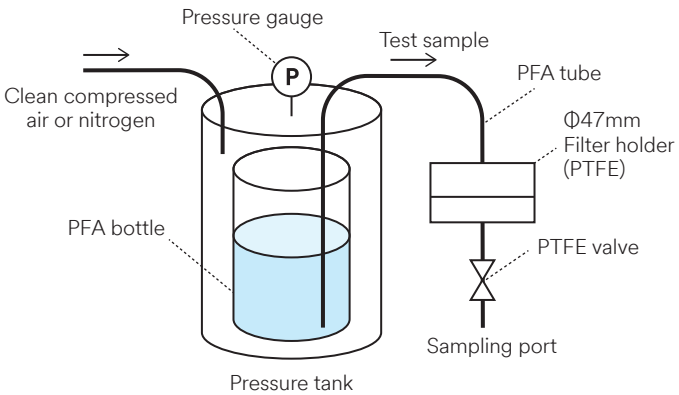

Figure 1: *Test set-up for challenging the ion exchange media*

3. Results

Flow Dynamic in Immobilized Ion Exchange Micro Bed

The flow dynamics of fluid through the immobilized porous ion exchange were studied with Computational Fluid Dynamics (CFD) analysis for two housing designs. These designs were based on the available housings commonly used in the industry. Design A which has the inlet and the outlet on the opposite length of the filter housing, also known as "in-line-style" and design B with both the inlet and the outlet at the same height and are known as T-style housings. These designs and the flow patterns through them containing the porous media are shown in Figure 2. Design B creates a condition that most of the flow concentrates through the top section of the porous media. The outcome would be that most of the media in the top half is consumed first leading to premature break through of the ions. In comparison, Design A allows even flow through the porous structure resulting in uniform and complete utilization of the ion exchange media. Design A is preferred for the porous ion exchange application as there is no equalizing factor at play similar to mechanical filtration where the pressure drop resulting from blocking pores acts as equalizing factor.

The Figure 3 shows the time sequence for filling the housing and the flow through the porous structure from 0.5 second to three seconds. Design A demonstrates uniform flow of the fluid into the housing and uniformly flowing through the porous structure. In contrast, Design B shows the fluid fills the housing non-uniform fashion resulting in non-uniform flow through the porous structure.

Metal Reduction Results

The results of metal reduction are shown in Figure 4. All metals were reduced either to single digit or double digit ppt levels from low ppb or high ppt levels. Both types of the ion exchange were effective in removing all metals. These results show very high effectives for these structures. This high effectiveness can be attributed to high surface area that presented by these structures as measured by BET to have 32.1 m^2/g and 27.1 m^2/g for the APP and SCP types, respectively.

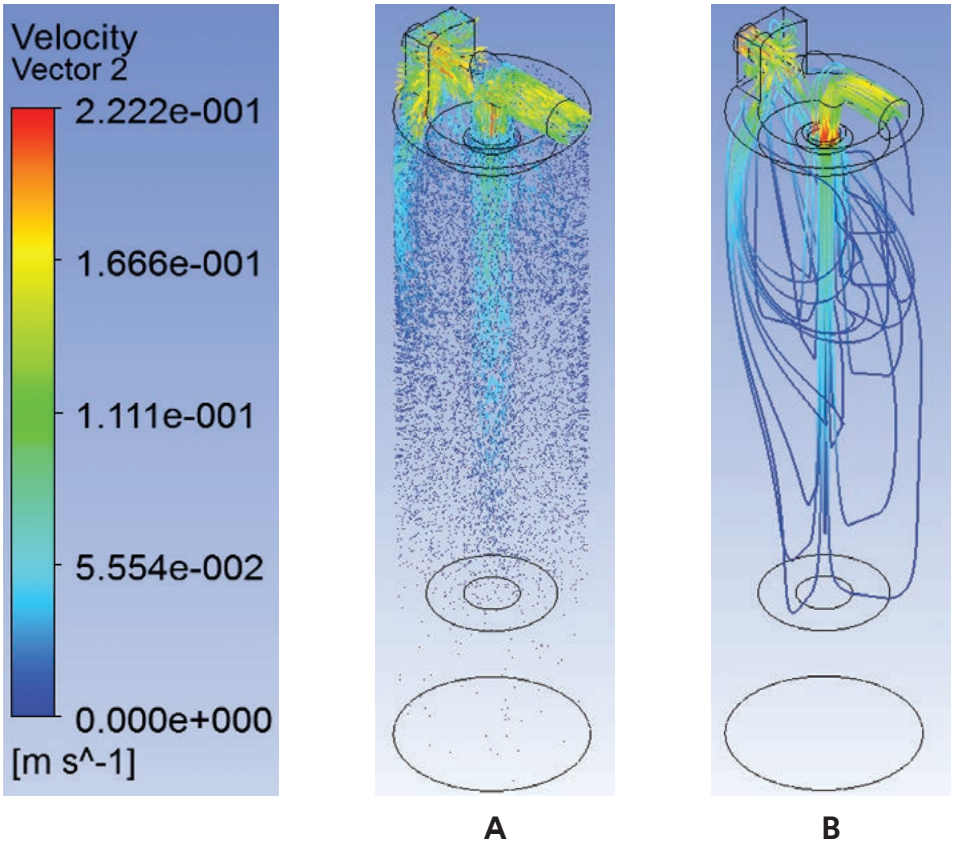

Figure 2: *Flow dynamic of fluid through housing Design A and design B and through the immobilized porous Ion exchange structure*

3. Results - continued

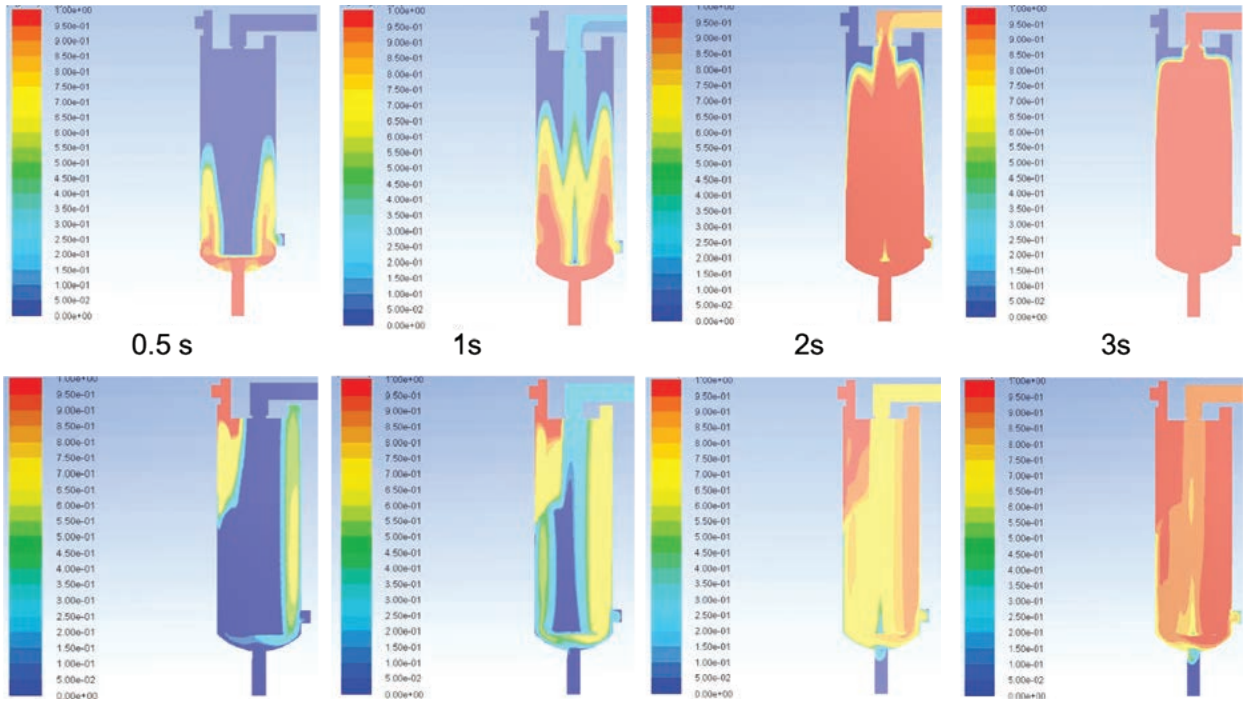

Figure 3: *Flow patterns for two housing designs. Time sequence for fluid flow into two housings, Design A with inlet and outlet on the same horizontal plane and Design B with the inlet and (b) outlet on opposite side or two horizontal planes.*

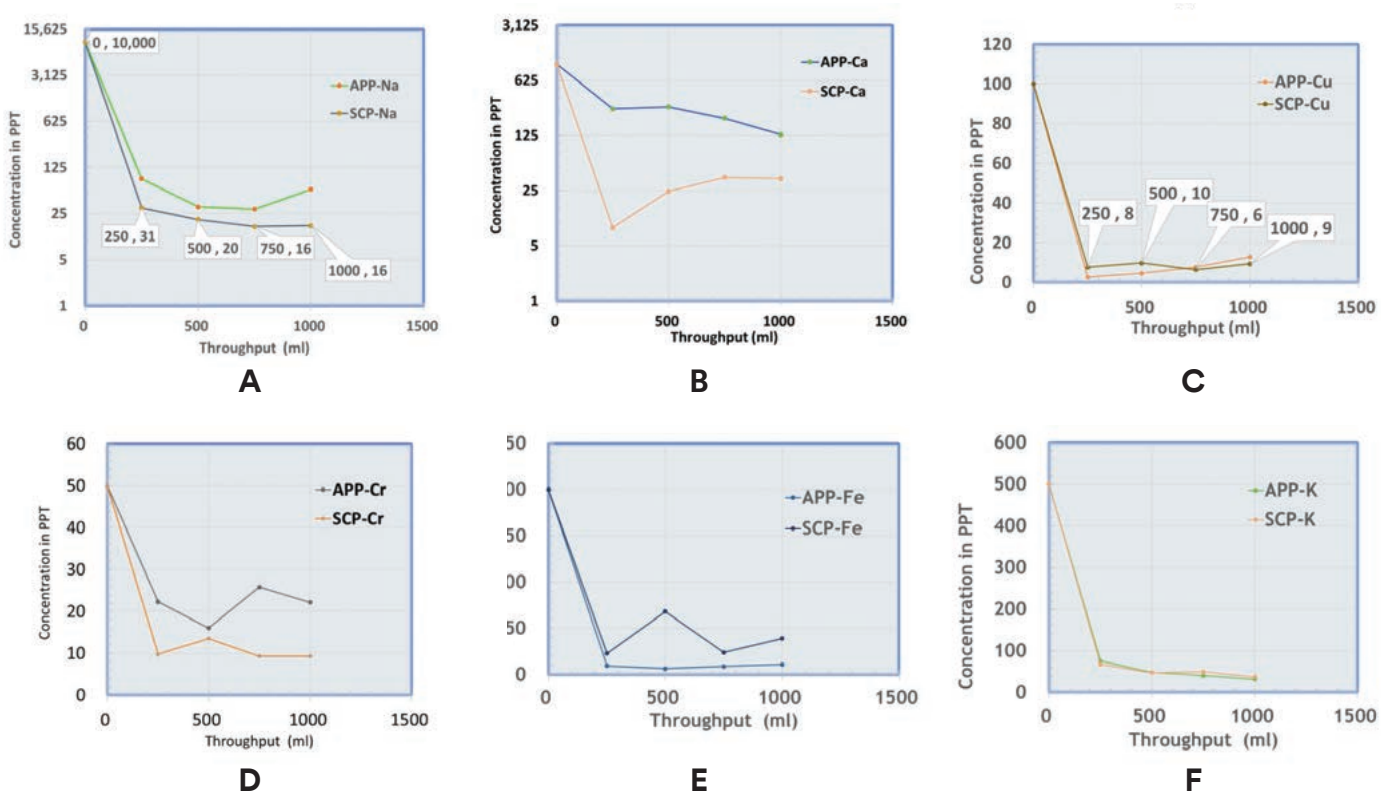

Figure 4: *Metal Analysis results as a function of throughput for (A) Na, (B) Ca, (C) Cu, (D) Cr, (E) Fe, and (F) K using two grades of ion exchange types of strong sulfonic acid (SCP) and Amino Phosphate (APP).*

4. Conclusion

The result of this study demonstrate that the 3M immobilized ion exchange resin technology can meet the new requirements for metal content in high purity chemicals. The use of an "in-line" style housing (bottom in, top out) optimizes utilization and capacity of the ion exchange media when compared with a "T-style" housing. The fixed pore structure contains high surface area micro channels which reduces the diffusion path allowing for proximity of the metal species to the active sites. The results of the studies presented in this paper demonstrate that the 3M immobilized ion exchange resin technology reduced metals content to single digit or low double digit ppt levels from low ppb or high ppt levels.

Acknowledgment

The authors would like to acknowledge the contribution of Nicole Petkovich for the BET analyses.

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3M Purification Inc.
3M Separation and Purification Sciences Division
400 Research Parkway, Meriden, CT 06450 USA

Phone 1-800-243-6894 1-203-237-5541
Web 3M.com/purification