Purification Method for Achieving Low Trace Metals in Ultra-High Purity Chemicals

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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 where the metal concentrations of low parts per billion (ppb) were effectively reduced to low parts per trillion (ppt). 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. 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

In recent years, the electronic devices have becoming more complex. The line / pattern size in electronic devices is 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 applications. The fluids are Ultra-Pure Water (UPW), etchants, cleaning solutions, Photoresists, developers, coatings, and Chemical Mechanical Planarization (CMP) slurries [1].

There are several purification methods that can be used for purifying fluids. These are evaporation, 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 controlled solely by the diffusion, which is dictated by the materials micro- and macro-structures [2]. 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 [3]. 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. New approach to improve diffusion is reducing the 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 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 increases mixing the likelihood of the species coming in contact with active surfaces. The 3MTM 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. Experimental

In this study, two types of 3MTM immobilized ion exchange resin products were evaluated, as shown in Fig. 1. One type is composed of strong acid cation exchange chemistry, identified as “SCP purifier”. The other type is based on a chelating chemistry and is identified as “APP purifier”. SCP and APP represent the model name of two types of 3MTM, Metal Ion Purifier, respectively. The products were cleaned by 3MTM purification technology.

Metals in organic solution were analyzed using Agilent 8900 ICP-QQQ instruments and metals in UPW were analyzed using Agilent 7900 ICP-MS instruments. System was washed with acid 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.

An effective surface area was measured in use of a Quantachrome (Anton-Parr) Autosorb IQ2-MP. 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 which defined by S. Brunauer, P.H. Emmett, and E. Teller.

The purifier was initially dry. The dry purifier was so wetted that the purifier works sufficiently. The dry purifier was soaked in an operating fluid. The purifier was mounted in a housing and flushed in minimum of 2 BVs (bed volume) with the fluid before a purification. In pre-conditioning test, 10-inch cartridge was soaked in UPW with the specific resistance of more than 18.2 MΩcm for 12 hours and flushed by 10 L of UPW. The UPW filtrate was collected in Perfluoroalkoxy alkane (PFA) bottles at 0 L, 6 L, 8 L, and 10 L. The metal concentration was analyzed by Agilent 7900 ICP-MS.

The schematic diagram for performance test was show in Fig. 2. Electronic-grade (EL-grade) 1-Methoxy-2-propanyl acetate (PGMEA) was transferred into an ultra-pure PFA vessel in a pressure tank and pushed through the system by increasing the pressure of the pressure tank.
purity air was used to pressurized and maintain a constant pressure. The test pressure was adjusted by a compressed air. The clean air was filtered to 0.003 μm rating to ensure no particulate was introduced into the fluid through the line. Prior to starting the test, the 2-inch purifier was installed into the high purity polytetrafluoroethylene (PTFE) housing and sealed to prevent any bypass or leaks. Downstream of the housing, a needle valve was installed for adjusting the flow rate. The 2-inch purifier were soaked in PGMEA for a minimum of 12 hours to ensure the structure is fully wetted by PGMEA and the air in the pores is replaced with the PGMEA in order to maximize the utilization of the ion exchange capacity. The purifier was flushed by 200 mL of PGMEA and was collected in high purity PFA bottles. After completion of the pre-conditioning, the PGMEA in the housing was emptied. The PGMEA spiked standard metal solution the initial 500 mL was discarded, and then subsequent filtrate was collected in high purity PFA bottles. The untreated sample was labeled as “Initial”. All the samples were sealed immediately after filling and opened only when ready for metal analysis by Agilent 8900 ICP-QQQ. More than twenty metal elements were analyzed to assess the effectiveness of each ion exchange chemistry. The metal concentration of spiked PGMEA was around 1 ppb.

3. Results and discussion

3.1 Reaction rate

Generally, the reversible reaction formular of an ion exchange resin is expressed by (1)

\[ \text{R-H} + \text{M}^+ \rightleftharpoons \text{R-M} + \text{H}^+ \] (1)

where \( \text{R-H} \) and \( \text{R-M} \) represents an ion exchange resin bonded with a hydrogen, H, and metal, M, respectively.

The forward reaction velocity \( v_f \) and the backward reaction velocity \( v_b \) are written by (2) and (3), respectively.

\[ v_f = \alpha [\text{R-H}] [\text{M}] \] (2)

\[ v_b = \beta [\text{R-M}] [\text{H}^+] \] (3)

where \( \alpha, \beta \) are reaction rate constant for forward and backward reaction, respectively, which strongly related to diffusion velocity in the ion exchange layer.

When fluid with metal ion \( \text{M}^+ \) passes through the ion exchange layer with the thickness \( \delta x \) at a liner velocity \( \delta x \) for \( \delta t \), as shown in Fig. 3. Here \( \delta x \) is the amount of the fluid which flowed for \( \delta t \) per a unit surface. A metal variation \( \delta \text{M}^+ \) is shown as

\[ \delta \text{M}^+ = \frac{\delta x}{\delta t} \]

Fig. 3. Schematic diagram of fluid flow passing through ion exchange layer.
\[ \delta M^+ = \delta t (v_f - v_h) = \left( \frac{\delta x}{LV} \right) (-\alpha [R-H][M^+] + \beta [R-M][H^+]) \] (4)

Initially, an ion exchange resin has initially a hydrogen form \([R-H]\). Then \([R-H] \gg [M^+], [R-M], [H^+]\)

\[ \delta M^+ / [M^+] \approx \left( \frac{\delta x}{LV} \right) (-\alpha [R-H]) \] (5)

Metal reduction ratio, \(\delta M^+ / [M^+]\), is proportional to \([R-H]\) and inversely proportional to \(LV\). Also, the metal concentration is a function of the depth, \(x\). Thus the thicker the ion exchange layer, the more is the metal reduction.

3MTM immobilized ion exchange resin technology enabled a purifier with thick ion exchange layer, i.e., depth purifier, as shown in Fig. 4. The depth purifier is more than 100 times as thick as membrane filters. The thick porous micro-channel microstructure enabled to increase. It is seemed that the depth is more effective than membrane filter for trace metal reduction.

While the extreme minimum metal ion concentration \([M^+]_{\text{min}}\) was obtained at \(\delta M^+ = 0\), that is,

\[ [M^+]_{\text{min}} = \left( \frac{\beta}{\alpha} \right) \frac{[R-M][H^+]}{[R-H]} \] (6)

The extreme minimum metal ion concentration \([M^+]_{\text{min}}\) depends on the metal concentration \([R-M]\). The depth filter may be able to achieve less minimum metal ion concentration \([M^+]_{\text{min}}\) than a membrane filter, because the depth filter can supply continuously a fresh layer of \([R-H]\) in the downstream. Also it is very important to reduce the initial metal contaminations, \([R-M]\), in ion exchange layer in order to lower the \([M^+]_{\text{min}}\). 3MTM purification technology enabled to reduce the metal extraction less than 50 ppt in UPW.

3.2. Surface area

The cross section of the 10-inch 3MTM Metal Ion Purifier was shown in Fig. 5. The purifier was tubular with around 15 mm thick and single open end (SOE) where the one end of the tubular was closed by flat end cap and the other end was open through 222-connector. The fluid flowed into from the tubular surface and came out from the connector. The outer surface area of the tube was about 0.05 m². The effective surface area of the purifier was measured by BET to have 32.1 m²/g and 27.1 m²/g for the purifier of the APP and SCP purifiers, respectively. The effective surface area of 10incher APP and SCP purifiers were about 8,000 m² and 7,500 m², respectively, which was extremely larger than the tube surface area. Therefore, it was clarified that the purifiers consisted of porous micro-channel microstructure.

3.3. Pre-conditioning

10-inch SCP was dry. The 10-inch SCP purifier was soaked in UPW for 12 hours and then flushed by UPW at the flow rate of 2 L/min. The other 10-inch
purifier was flushed without soaking. The total trace metal concentration in the filtrate was analyzed by Agilent 7900 ICP-MS, as shown in Fig. 6. The total metal of both SCP purifiers was less than 50 ppt after flushing of 6 L. It was supposed that the low trace metal extraction was owed to increasing contact between the fluid and the active surface by using smaller pore sizes, increasing number of pores, and lengthening of the porous structure. It was clear that 3M™ purification technology could achieve the very high pure SCP purifier with trace metal extraction less than 50 ppt by the increasing contact. The most initial extraction was sodium which seemed to come from the environment and washed out by flushing.

APP purifiers were also flushed in the same manner. The total trace metal was in accordingly with flushing throughput, as shown in Fig. 7. The total metal for the purifier with soaking was less than 50 ppt after flushing of 6 L, while the total metal for the purifier without soaking could not achieve less than 50 ppt even after flushing of 10 L. It is seemed that APP is a little bit slower to be swelled than SCP. It was necessary to swell sufficiently 3M™ Metal Ion Purifier before applying to fluids. It was recommended that the 3M™ Metal Ion Purifier could be swelled sufficiently and flushing.

3.4. Flushing with PGMEA

2-inch purifiers were soaked in PGMEA for 12 hours and then flushed with PGMEA. The trace metal concentration in the filtrate was analyzed by
Agilent 8900 ICP-QQQ. The difference of trace metal concentration in filtrate from the initial PGMEA was shown in Fig. 8. The negative means the reduction from the initial concentration. Any metal extraction from both purifiers of APP and SCP was not observed.

3.5. Metal reduction results

A PGMEA was spiked by metal standard solution so that metal concentration was around 1 ppb. The PGMEA was filtrated by 3M™ Metal Ion Purifier. The results of metal reduction were shown in Fig. 9. The metals less than the quantitative limit of 10 ppt was not shown in Fig. 9. 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 trace metals. It was found that the SCP purifier could remove more sodium than the APP purifier, while the APP purifier could remove more iron than the SCP Purifier. It was supposed that the difference is came from the ion exchange spices of the APP and SCP purifier. The APP and SCP purifier could compensate each other for trace metal reduction.

4. Conclusion

The fixed pore structure in 3M™ Metal Ion Purifier contains high surface area micro channels which reduces the diffusion path allowing for proximity of the metal species to the active sites and
which achieves high cleanness of the active sites. The results of the studies presented in this paper demonstrate that the 3M™ immobilized ion exchange resin technology and purification technology can meet the new requirements for trace metals in high purity chemicals to single digit or low double digit ppt levels from low ppb or high ppt levels.

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