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Metal Reduction from Highly Viscose Microelectronics Fluids

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ABSTRACT

Various chemicals are used in photo-resists applications that have high viscosity. The metal content of these chemicals is of concern as they may contaminate the wafers during the processing and post processing by diffusing into the circuit components and affecting their performance over time.

The high viscosity of these chemicals results in high pressure drop across porous media such as membranes or monoliths. A new monolith microstructure has been developed allowing to process high viscosity fluids for metal reduction while maintaining high flow rates.

Experiments were performed to compare the flow rates and the metal reduction of the monoliths. In addition, the metal reduction capacities were compared. The results of metal reduction will be presented using the new monolith.

Keywords: Purification, Filtration, Defect reduction, Photoresist, High Purity Chemicals

1. INTRODUCTION

High Purity fluids and gels are needed for various microelectronics applications [1]. These fluids could be high polymer solutions, epoxies, amines, photoresists, masks, barrier layers, etc. The low metal content of these fluids is of prime importance as the metals interfere with the main functions such as conductivity, resistance, capacitance, dielectric, or others[2]. Purification methods such as distillation cannot by employed for these high solid solutions as it leads to phase separation. The Ion exchange technology can be used. However, the packed bed of the ion-exchange beads is not very efficient, needing a large volume of beads and difficult to reach low parts per trillion. There are also membranes with grafted ion-exchange properties that can be used for removing metals. These membranes have pore sizes that are smaller than one micron. These structures are associated with high pressure drops when used for high viscosity fluids. The flow of high viscosity fluids through depth porous structures has been studies[3]. The combination of viscose flow in porous structures with ion exchange properties are not well known. The objective of this study was to develop structures that can operate high viscosity fluids at high flow rates while efficiently removing metal ions.

2. EXPERIMENTAL PROCEDURES

Two ion-exchange chemistries were made into monoliths with different pore structures. The two ion-exchange chemistries were sulphonic acid and amino phosphate. The sulphonic acid chemistry is a strong cationic ion-exchange with H ion for exchange denoted as SCP while the ammino phosphate is a chelating chemistry also with H ions for exchange denoted as APP. These chemistries were made into monoliths with two different densities. One monolith would be denser with smaller mean pore size known as MIP-UHP SCP or MIP-UHP APP and the other less dense with larger mean pore size known as MIP-HV SCP and MIP-HV APP. These structures were subjected to fluids at various viscosities and upstream pressures and measured the flow rates at each viscosity and pressure. In addition, PGMEA was spiked with common metals of interest in the microelectronics manufacturing and passed through the monolith and measured the metal removal capability of the two chemistries. The metal content of the spiked and the purified samples were analyzed using ICP-MS.

2. RESULTS AND DISCUSSION

The results of the flow rate at various viscosity and various pressure setting are listed in figure 1. The samples listed as UHP are tighter media and a typical ion-exchange capacity of 450 mEq per 10” cartridge while, the HV samples have more open structures with a typical ion-exchange capacity of 250 mEq per 10” cartridge.

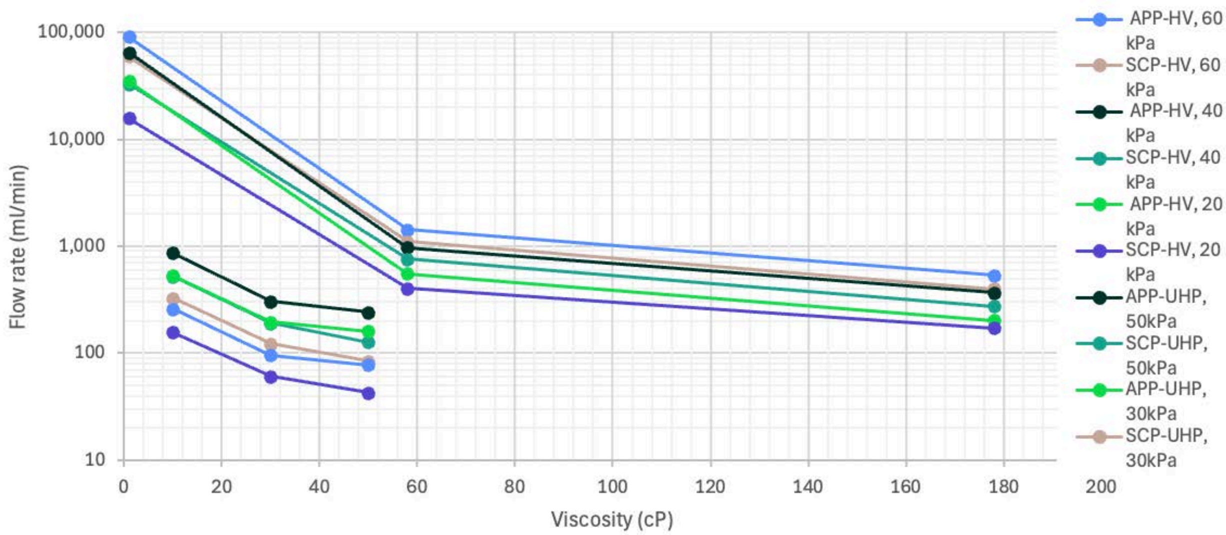

Figure 1. Flow rate versus pressure at various viscosities

The effect of increasing viscosity on flow rate is significant. The relationship between these two factors is a negative exponential meaning that the flow rate will be reduced exponentially by increasing the viscosity. For the UHP grade, the flow rate at viscosities larger than 50 cP is not practical as the flow rate drops to less than 100 ml/min per 10” cartridge. In comparison, the HV grades can operate at 10 times faster flow rate at comparable upstream pressures. For fluids with viscosities higher than 50 cP, both the SCP and APP in the UHP format did not result meaningful flow rate for a 10” cartridge.

Higher flow rates are seen when the pressure across the monoliths is increased across of any monolith grade. However, the increase in flow rate because of increase in pressure drop is not as pronounced as lowering the viscosity. There is a linear relationship between the increase pressure drop and the flow rate. This behavior is shown in figure 2.

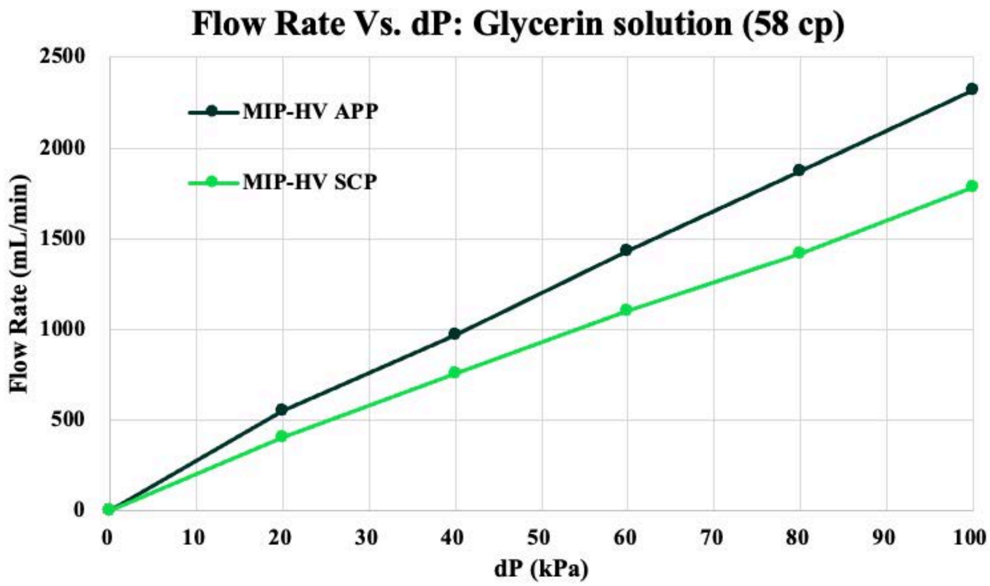

Figure 2. The Flow rate versus pressure drop across MIP-HV SCP and APP monoliths at 58 cP

Metal Removal Efficiency:

The metal removal efficiency of both structures with either chemistry was assessed. The results are summarized in figure 3 through 6. Both MIP HV and MIP UHP demonstrated a high removal efficiency of >90% for total metal ion contamination in PGMEA. The results of metal removal using the low-density MIP HV with the two chemistries of SCP and APP, exhibit varying affinities towards different metals. The APP chemistry is more effective in removing heavier metals with higher valance (e.g. Mg, Ca) while the SCP chemistry shows more effective at removal of lighter metals that are monovalent. The denser structure of MIP UHP with both chemistry shows very effective removal of all metals.

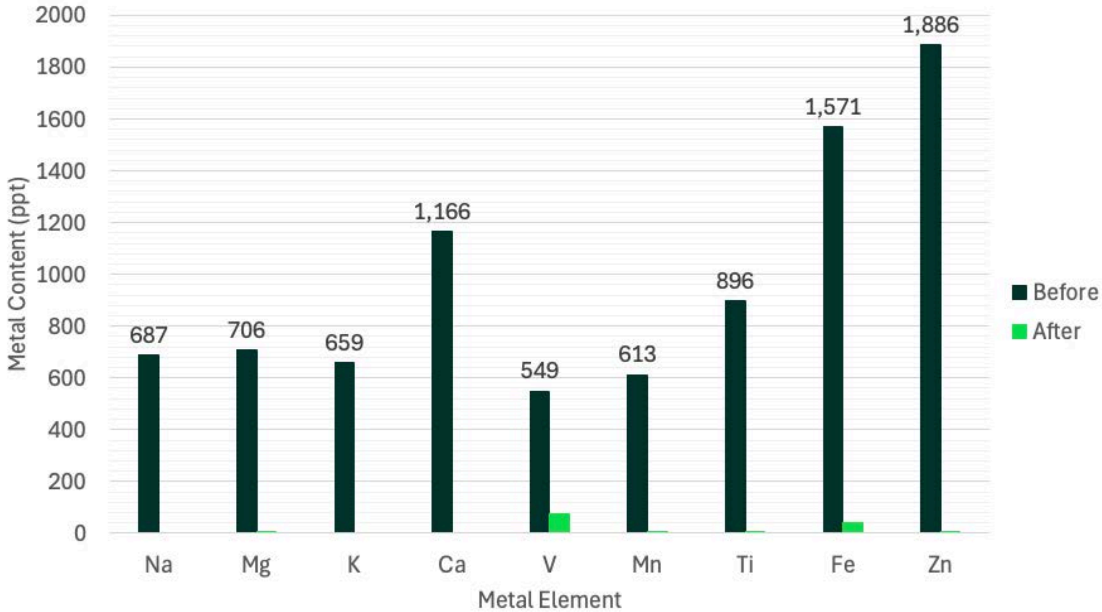

Figure 3. Metal removal form PGMEA by single pass using MIP-HV SCP grade (2.0 L/min)

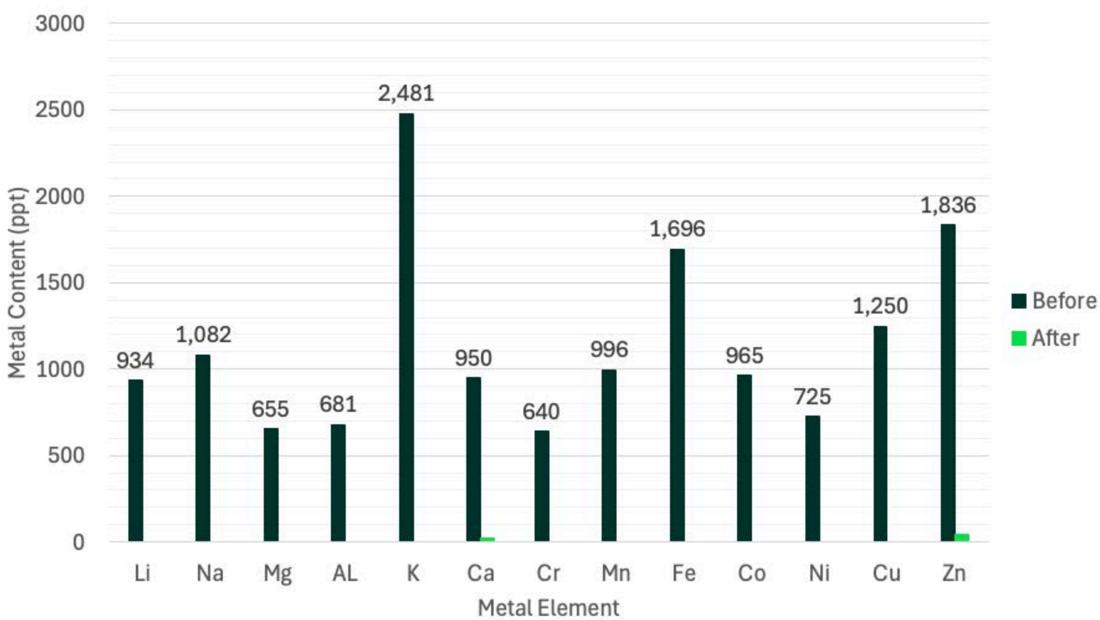

Figure 4. Metal removal form PGMEA by single pass using MIP-UHP SCP grade (0.7 L/min)

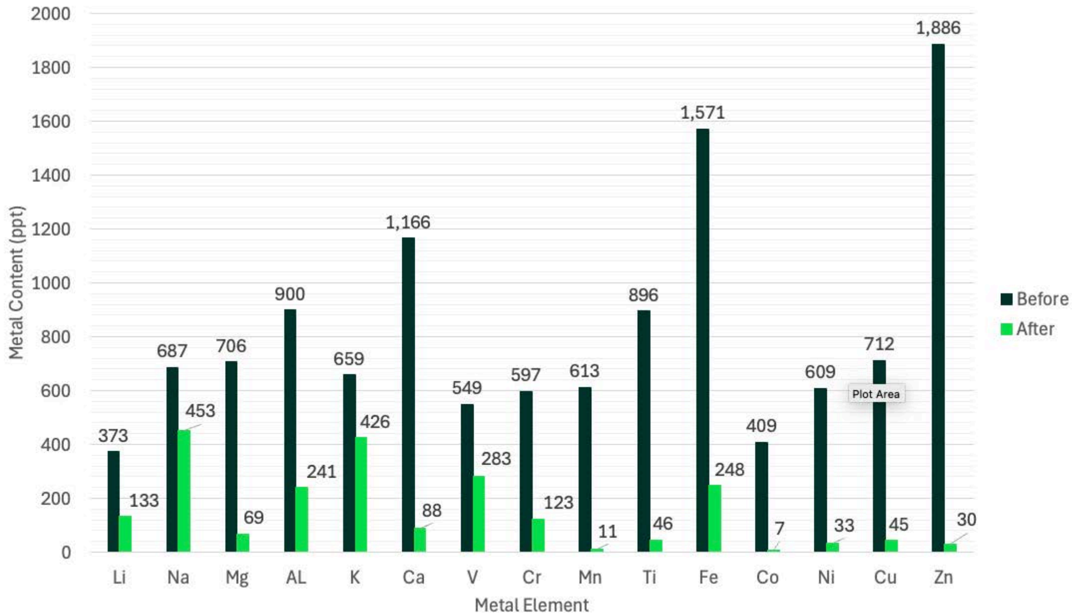

Figure 5. Metal removal form PGMEA by single pass using MIP-HV APP grade (2.0 L/min)

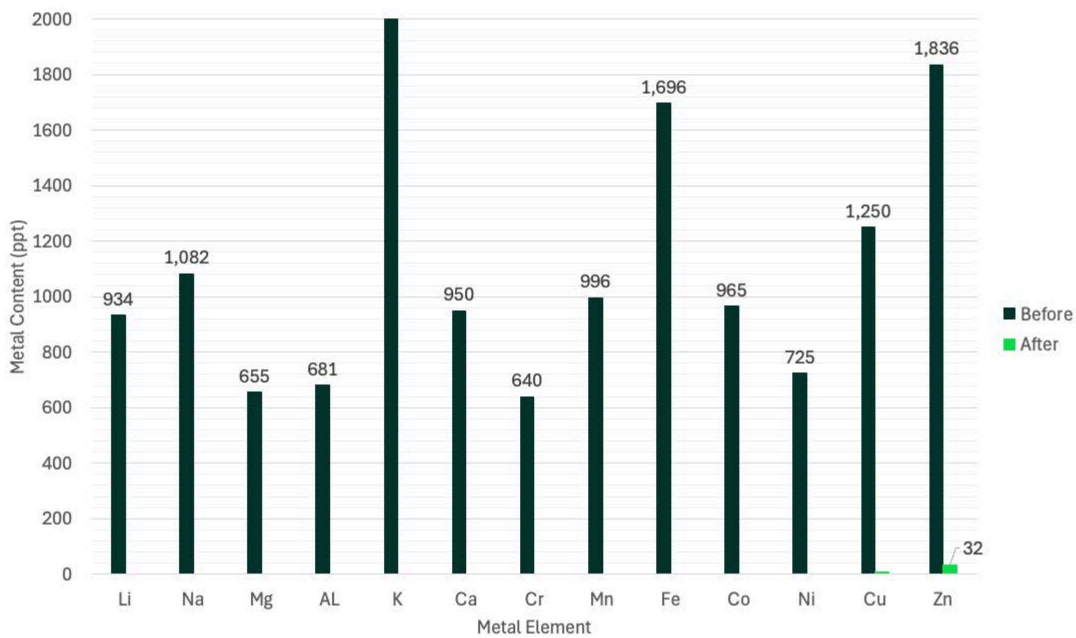

Figure 6. Metal removal form PGMEA by single pass using MIP-UHP APP grade (0.7 L/min)

CONCLUSIONS

The high viscosity fluids are used in the manufacturing process of the integrated circuits. These fluids have metal impurities which if not removed could cause functional and reliability issues. There are very limited options for removing metals from these fluids. Two ion exchange chemistries were made into depth porous structures that could flow reasonably well and reducing metal content. Both ion exchange chemistries of strong sulphonic acid (SCP) and ammino-phosphate (APP) were effective for removing metals from PGMEA. The SCP chemistry showed capability for removal of most metals while the APP chemistry was more efficient at removing the heavier metals that are multi-valent.

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