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The Effect of Membrane Surface Charge on Filtration of Ceria CMP Slurry

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The Effect of Membrane Surface Charge on Filtration of Ceria CMP Slurry

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Abstract

Proper filtration of CMP slurries is critical for the effective manufacture of semiconductor devices. As current node size approaches single digit nanometers, CMP slurries with a particle size range within double digit nanometers is becoming mandatory.

Traditional polypropylene non-wovens, while a commonly used media for CMP slurry filtration, are ineffective for large particulate filtration when the slurry mean particle size is less than 50 nanometers. In contrast, various membranes can be produced with defined pore sizes with high accuracy. Nonwovens are based on particle retention of log reduction values of 2 or 3, while membranes are rated based on the bacteria retention with log reduction values of 5 or higher. For these reasons, polypropylene nonwovens were omitted from this filtration study.

In this study, three different membranes with 0.65 um pore size ratings, but differing Zeta potential, were tested with an acidic ceria slurry of pH 3. Specifically, these three membranes consisted of: a) nylon with a positive Zeta potential b) polyethersulphone with a neutral Zeta potential and c) polyethersulphone with a negative Zeta potential.

The ceria slurry filtered through these three membranes was collected and subjected to particle size analysis at the 0.25-1 um range. The data indicated that two particle removal mechanisms were likely present: absorption and mechanical filtration. Further, while absorption seemed to occur in every instance, the duration of the absorption differed significantly.

This paper will present the filtration results of each membrane, from initial breakthrough to filtration over several minutes. The surface energy and surface chemistry of the membranes on processing of the CMP slurries will be discussed in detail.

1 Introduction

The Chemical Mechanical Planarization (CMP) process has been developed to enable increasingly finer nodes. Filtration has a critical role in the control of Large Particle Counts (LPC) and the reduction of defects associated with them. CMP slurries are complex colloidal chemistries with charge balances that hold particles in suspension. This promotes the avoidance of agglomerations and settling of particles within a CMP slurry. Changes in charge balance can alter the characteristics of a CMP slurry. These changes are prompted by variation in chemistry or interactions with other surfaces having a different charge status.

The filter is one component that a CMP slurry encounters. The filter has a high surface area due to its porous microstructure. Thus, it is critical to understand the potential interactions between the filter and a CMP slurry to ensure that the charge difference does not alter the characteristics of the slurry. A charge difference between the filter and a CMP slurry may also lead to absorption of particles by the filter. [1]

1.1 Zeta Potential Theory

Electrokinetic effects like zeta potential can be determined with four different measurement techniques:

- Streaming potential
- Electrophoresis
- Electroosmosis
- Sedimentation potential

Streaming potential and electrophoresis are the two most common techniques. Streaming potential is typically used for the determination of zeta potential of larger surfaces (diameter >25 µm) and electrophoretic methods like electrophoretic light scattering are applied for measuring zeta potential of particles with a diameter of up to 100 µm.
Measurements of the streaming potential are applied for macroscopic surfaces, where samples are mounted on sample holders and form a capillary flow channel. Upon relative movement of the liquid with respect to the solid sample, the ions of the electrochemical double-layer are sheared off their equilibrium position and shifted along the solid surface. The resulting charge separation gives rise to

electrokinetic effects, one of these is called streaming potential. The streaming potential, or alternatively streaming current data, is used to calculate zeta potential.

The fundamental equations that relate the streaming potential and the streaming current to zeta potential have been derived by Hermann von Helmholtz and Marjan von Smoluchowski. The equation used for the calculation of zeta potential using streaming current data requires exact knowledge about the length and cross-section of the streaming channel, i.e. solid sample size.

$$\zeta = \frac{dl}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A}$$

Equation 1

ζ: Zeta potential
dl/dp: slope of streaming current vs. differential pressure
η: electrolyte viscosity
ε: dielectric coefficient of electrolyte
ε_0: permittivity
L: length of the streaming channel
A: cross-section of the streaming channel

2 Experimental Procedure

2.1 Zeta Potential Measurements

In this study, zeta potential measurements were measured with the SurPASS equipment from Anton Paar (streaming potential)[2]. The SurPASS equipment contains a pump that provides a driving force to apply pressure, and the differential pressure is monitored at 400 mbar.

For the test, a gap cell with a 20 x 10 mm sample holder, which provides data on L and A to fill equation 1. Electrolyte viscosity (η), dielectric coefficient (ε) and electrolyte permittivity (ε_0) are also set with the solution, used as explained below.

The beaker was filled with 500 millilitres of water (Milli-Q water). Conductivity was adjusted to 14 – 15 mS/m with potassium chloride (KCl) powder. The solution was fixed at pH 3, by adding 5 grams of hydrochloric acid (HCl) 0,1N to the solution.

Each membrane and nonwoven were attached to the sample holder via double-sided adhesive tape. An adjustable gap cell was used. Prior to starting measurements: a) 100 ml of the prepared solution was purged through the system (machine and samples), then discarded. b) the gap was set in the gap cell to 100 ± 5 µm. c) a flow check was performed to ensure the flow/pressure ratio was correct for each side of the gap cell.

After a positive flow check, the measurement was initiated. The zeta potential data was then collected between pH 3 and 8. To modify pH, a 0.05N potassium hydroxide solution was used, via automatic injection into the system after each measurement. A curve for each material was saved.

These membranes were then subjected to CMP filtration to illustrate the effect of the membrane charge.

2.2 CMP Filtration Test

The three 0.65 um membranes of differing Zeta potential were exposed to individual filtrations of acidic ceria CMP slurry of pH 3.

To achieve this, a 5-gallon tote of raw CMP slurry was agitated via gyroscopic mixing. 2 mL of the slurry was then added to DI water to create a 6-liter CMP solution. This solution was continually mixed via magnetic stir plate and processed through each filter at a representative flow rate via diaphragm pump. The output of the pump was calibrated by adjusting its RPM while measuring CMP slurry with a graduated cylinder and stopwatch.

Effluent samples were collected five separate times during 11 minutes of filtration. The total filtration time and selected intervals of sample collection were determined based on the effective filtration area of a 47mm disc and its anticipated transition time between absorption and mechanical removal functions. An unfiltered slurry solution sample was also collected.

All collected samples were subjected to particle size and distribution analysis at the 0.25-1 um range via the FX-Nano 780 AD from Particle Sizing Systems. Differential pressure was recorded during all testing and turbidity analysis was conducted on all samples.

3 Results and Discussions

The results of zeta potential for the four filter materials used in this filtration study are shown in figure 1-3. These samples were selected to have a positive, negative, or neutral zeta potential when compared to a CMP slurry with pH 3. Specifically, these materials consisted of: a nylon membrane that exhibited positive zeta potential, a polyether sulfone (PES) membrane that exhibited negative zeta potential, and another PES membrane that exhibited neutral zeta potential.

All filter media were challenged with ceria slurry at like process conditions and particle counts were measured before and after the filter media. Filter efficiency for particle sizes ranging from 0.25 um to 1 um are shown in figure 4-10.

At the 0.25 um range, the PES membrane with negative zeta potential removes almost all particles. The nylon membrane with positive zeta potential initially removes most particles, but removal efficiency drops rapidly. The PES membrane with relatively neutral zeta potential shows some initial particle removal, however, the removal efficiency declines drastically.

100 percent removal of the 0.25 um particles by the filter with negative zeta potential indicates that the removal mechanism cannot be mechanical. It is believed that the removal in this instance is via absorption. Note that the absorption removal mechanism remains strong even after 10 minutes of filtration. The same behaviour is not observed with the nylon membrane, which is positively charged compared to the slurry pH. It is believed that because both the particles and the membrane are positively charged at pH 3, the two surfaces repel each other. Thus, the absorption removal mechanism would be minimal.

At the 0.3 um range, the absorption removal mechanism of the negatively charged PES media is still active as 0.3 um particles are removed at high efficiency. For the other media, a low percentage of 0.3 um particles are removed, seemingly via mechanical screen. For particles larger than 0.3 um, similar behaviour for the negatively charged PES media is observed. Specifically, the absorption mechanism is still very strong, and particles are removed at very high efficiency. In general, as the particle size range of interest increases, the mechanical filtration efficiency also increases.

For CMP slurry filtration, selecting a material with neutral zeta potential is ideal. This will result in the prevention of absorbance of fine particulate. The next best option is to select a material with a zeta potential that matches the pH of the slurry. If the slurry pH is less than 7, a filter media with positive zeta potential should be selected. If the slurry pH is higher than 7, a filter media with negative zeta potential should be selected.

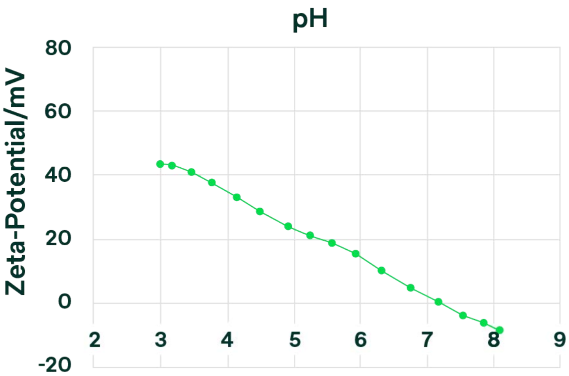

Figure 1. Zeta potential of a nylon membrane rated 0.65 um

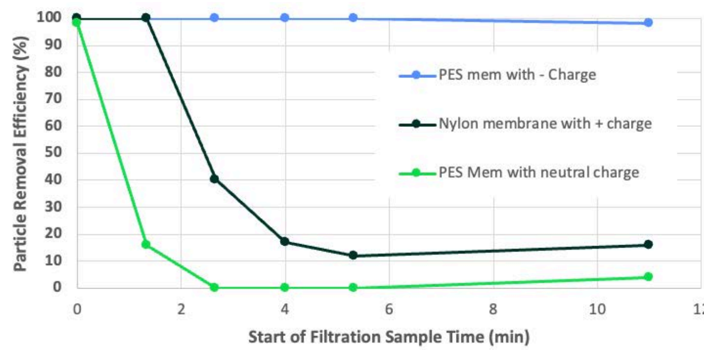

Figure 4. Filtration efficiency at 0.25 um particles.

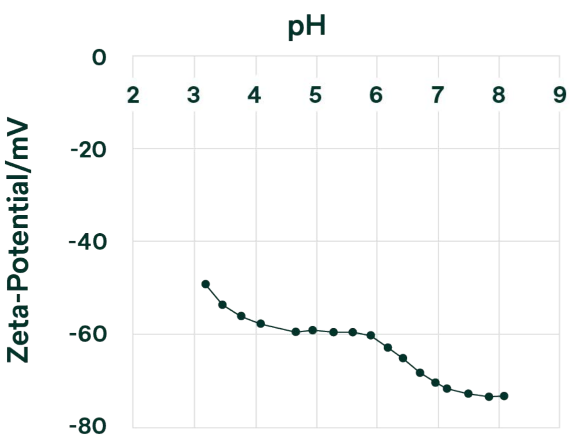

Figure 2. Zeta potential of a PES membrane rated 0.65 um

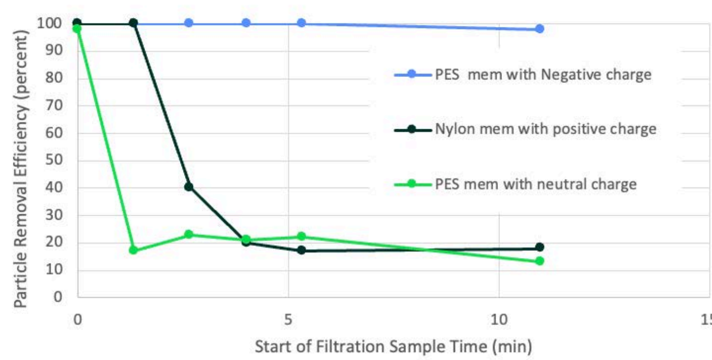

Figure 5. Filtration efficiency for 0.3 um particles.

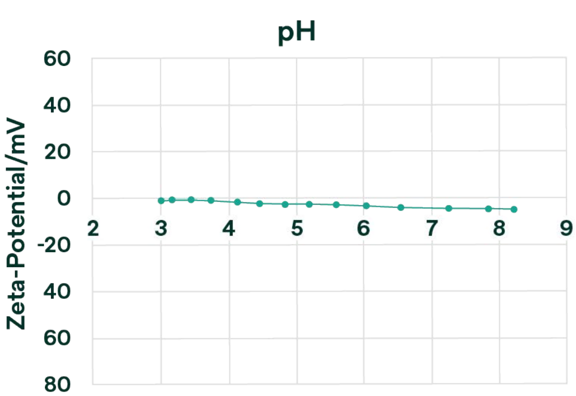

Figure 3. Zeta potential of another PES membrane rated 0.65 um

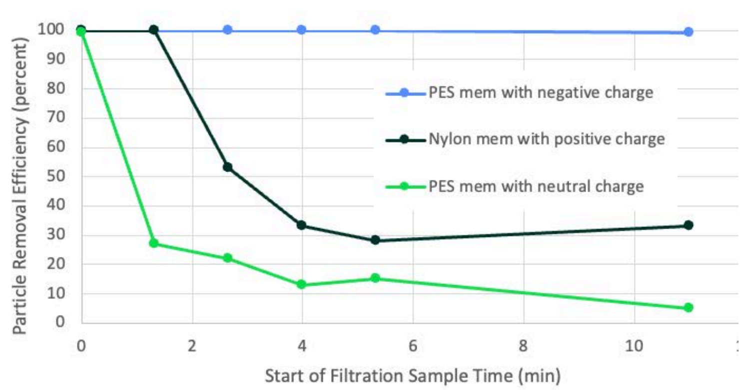

Figure 6. Filtration efficiency for 0.4 um particles

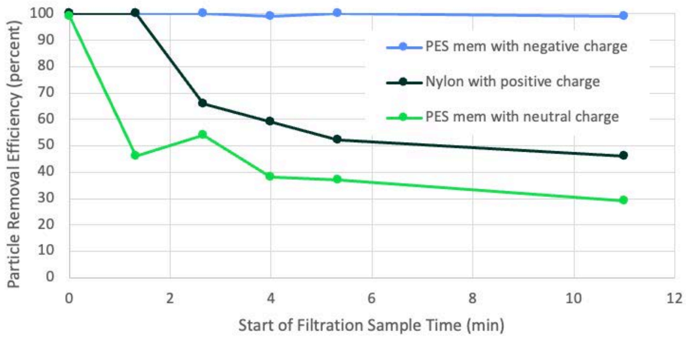

Figure 7. Filtration efficiency for 0.5 um particles

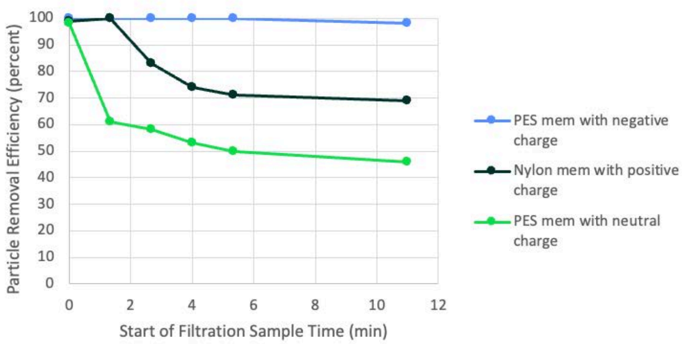

Figure 8. Filtration efficiency of 0.6 um particles.

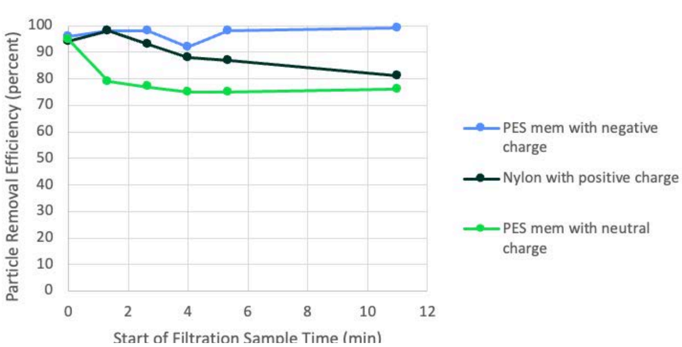

Figure 9. Filtration efficiency of 0.73 um particles

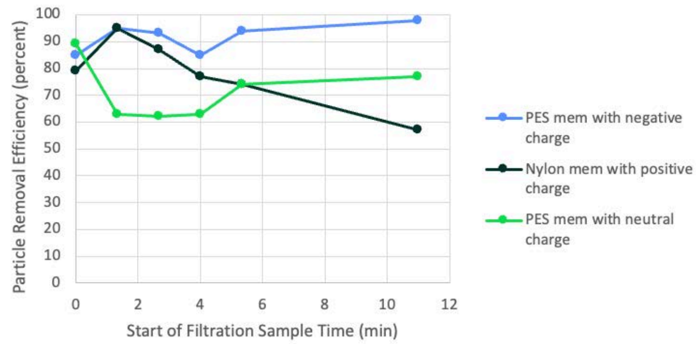

Figure 10. Filtration efficiency of 1.04 um particles.

4 Conclusions

The charge of the filter with various zeta potentials has a significant impact on initial filtration. The comparison of the filter zeta potential as a function of pH with the slurry pH could be used as a guide for filter selection.

When the slurry pH is less than 7 and the filter is negatively charged at that pH, there will be significant absorption which is not preferred for CMP slurry classification filtration. Slurry particles irrespective of their sizes are removed from the slurry. However, it is more pronounced for smaller particles which have smaller mass.

When the slurry pH is less than 7 and the filter is positively charged at that pH, there will be some initial absorption. While not the most preferred CMP slurry classification filtration technique, the adverse effects are not nearly as detrimental as compared to using negatively charged membrane at this pH.

Similar logic applies in cases where the slurry pH is greater than 7. Specifically, it is more advantageous to use a filter with a negative charge in this instance to avoid absorption as a primary removal mechanism.

Finally, the ideal filter choice appears to be one that exhibits neutral charge at the slurry pH. This will avoid any unintended interference with the charge neutrality of the slurry, which may result in undesirable removal of effective slurry particles.

5 References

[1] Arnold, T. "Fluid purification using charge-modified depth filtration media." Bioprocess Int 3.10 (2005): 44-49.

[2] Luxbacher, T (2014). The Zeta Guide: principles of the streaming potential technique. Anton Paar GmbH: Graz, Austria.

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