Proper Filtration Removes Oversized Particles from CMP Slurry Systems

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Abstract
Single stage recirculation filtrations were performed to remove oversized particles from colloidal silica based Chemical Mechanical Polishing (CMP) slurries. Proper filtration was demonstrated to achieve rapid removal of oversized particles while not altering the percent solids of the CMP slurry. Mathematical models were developed to simulate particle reduction in CMP slurry distribution systems. The models predict particle concentration as a function of the flow rate, the particle removal efficiency of the filter, and filtration time. The models show that flow rate is the most critical parameter in order to achieve rapid removal of oversized particles. The major role of pre-filtration is to capture a portion of the oversized particles and protect the final filtration from premature plugging in order to deliver maximum filter service life.

Based on examination of the limited data, the recirculation flow model adequately predicts the particle concentration profile. Ultimately, selection of the optimum filters depends on flow rate, particle removal efficiency of the filter, filtration scheme (single vs. multi-stage filtration), and filter service life.

Introduction
For microelectronics applications, CMP slurries have a well defined particle size distribution and are often composed of fine abrasive particles up to 0.25 µm. A small population of oversized particles greater than 0.5 µm is typically found in a CMP slurry system. Oversized particles can result from particle agglomeration, drying of slurry from wetted surfaces, interactions within the slurry distribution system, and introduction of contaminants from handling. These oversized particles affect the level of defectivity on the surface of the wafer after CMP has been completed. Filtration has been shown to be effective in removing oversized particles from copper CMP slurries, resulting in a reduction of micro-scratches on the surface of the polished wafer. Hence, filtration has been incorporated into the CMP process for improved yield management during the manufacturing of integrated circuits.

This study investigates the effectiveness of several filtration modes on the removal of oversized particles from silica based copper CMP slurries and the consistency of solids content before and after filtration. In addition, a mathematical model has been developed to simulate particle reduction in a CMP slurry distribution system when the filtration system is being operated under recirculation mode. The filtration results of the reduction in oversized particle concentration were used to evaluate the particle concentration profile predicted by the mathematical model.

Experimental
A colloidal silica based CMP slurry of approximately 50% solids was obtained from a commercial source. To simulate a low percent solids slurry, the 50% solids slurry was diluted to 1:~160 ratio using DI water filtered through a 0.1 µm membrane filter. The resulting particle count was approximately in the range of 1,000,000 particles/mL @ ≥0.54 µm. The diluted slurry samples were tested and filtered through all polypropylene (PP) depth filters. Filters tested included Betapure™ CMP series filters, and some competitive PP filters with micron ratings ranging from 0.5 to 10 µm. Filtration experiments were performed via single stage, recirculation mode filtrations under constant pressure. Influent and effluent samples at different filtration times were collected for particle sizing and counting, and percent solids determination.

The CMP slurry filtration test stand consisted of a pump to deliver fluid from a reservoir to a series of 316 stainless steel filter housings. Pressure gauges were installed before and after each of the filter housings to monitor differential pressure during filtration. Sanitary connections and 316 stainless steel pipe were used for ease of cleaning. Prior to carrying out any filtration experiment, the CMP slurry filtration test stand was flushed and cleaned with DI water filtered through a 0.1 µm membrane filter. The residual DI water was allowed to drain from the filtration test system and a 0.5 µm filter was installed in the last filter housing. Then, filtered DI water was drawn from a 5 gallon reservoir and fed to the 0.5 µm loaded filtration test stand. To make sure that there was no oversized particle contribution from the test system, this operation was run under recirculation mode until the particle count reached an acceptable level, <50 particles/mL @ ≥0.5 µm. Once the test stand was cleaned, it was ready for the CMP filtration experiment. A 5 gallon batch size was used for the CMP slurry filtration.

Particle size analysis for particles greater than 0.5 µm was performed via Accusizer Model 780A by Particle Sizing Systems. The background particle count was maintained at <50 particle/mL @ ≥0.5 µm throughout the sample analysis by flushing with filtered DI water. The counting threshold was set at 2000 particles/mL @ ≥0.5 µm.

Determination of percent solids was performed using Inductively Coupled Spectroscopy (ICP). Using an ICP Si standard of 10,000 ppm, successive dilutions with DI water were used to prepare 100, 10, 1, and 0.1 ppm standards for calibration. The actual silicon concentrations were 100.382, 10.437, 0.944, and 0.159 ppm for the 100, 10, 1, and 0.1 ppm standards, respectively. Based on the ICP responses, 1.0 ppm may be regarded as the limit of quantitation (LOQ). Figure 1 shows the expected versus actual silicon concentration as determined by ICP.

To further reduce the uncertainty in measuring the content of Si, the influent and effluent samples were diluted with DI water to the upper range of the calibration curve, i.e., between 80 and 90 ppm for ICP analysis. The Si determination was performed in triplicate and the average values were reported. The resulting Si readings were converted to SiO₂ and reported as percent solids.
Model Development

It is not uncommon for facility engineers to perform filtration on a tote in a closed loop system until oversized particle counts are reduced to an acceptable level prior to transferring slurry from the tote to the day tank in a CMP distribution system. Figure 2 represents a simplified flow schematic of a closed loop recirculation slurry system with two stage filtration.

The mass balance of particle concentration as a function of time, \( t \), of the closed filtration loop leads to a first order differential equation as follows.

\[
V \left( \frac{dC}{dt} \right) = Q \left( C_2 - C \right) \quad \text{Eq. (1)}
\]

where \( C_2 = C_1 \left( 1 - \varepsilon_2 \right) \) \quad \text{Eq. (2)}

\[
C_1 = C \left( 1 - \varepsilon_1 \right) \quad \text{Eq. (3)}
\]

\[
C = C_0 \quad \text{at} \quad t = 0 \quad \text{Eq. (4)}
\]

Assuming, constant filtration efficiency \( \varepsilon_1 \) and \( \varepsilon_2 \) and uniform particle concentration, \( C \), in the system, then the normalized particle concentration \( C/C_0 \) in the tank of volume, \( V \), would follow the relationship:

\[
\frac{C}{C_0} = e^{-\xi \left[ t/(V/Q) \right]} = e^{-\xi \left( t/\tau \right)} \quad \text{Eq. (5)}
\]

and

\[
\xi = \varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2 \quad \text{Eq. (6)}
\]

\[
\tau = V/Q \quad \text{Eq. (7)}
\]

Where \( C_0 \) is the initial particle concentration prior to filtration and \( \tau \) is a time constant and defined as a ratio of tank volume to flow rate. The physical significance of \( \tau \) is that it represents average residence time of particles in the tank. The term \( t/\tau \) represents the number of bath turnovers for a given filtration time, \( t \). Consider a special case where single stage filtration with filtration efficiency, \( \varepsilon_1 \), is incorporated in the system. Then, Eq. (5) reduces to

\[
\frac{C}{C_0} = e^{-\varepsilon \left( t/\tau \right)} \quad \text{Eq. (8)}
\]

Let’s consider two single stage filtrations having a particle removal efficiency of \( \varepsilon_1 \) and \( \varepsilon_2 \), respectively. To have the same particle concentration profile for these two single stage filtrations at a given filtration time, a relationship can be derived between the filter efficiency and flow rate from Eq. (6) as follows.

\[
\frac{C}{C_0} = \exp \left[ -\varepsilon_1 \left( t/\tau_1 \right) \right] = \exp \left[ -\varepsilon_2 \left( t/\tau_2 \right) \right] \quad \text{Eq. (9)}
\]

\[
\varepsilon_1 \left( t/\tau_1 \right) = \varepsilon_2 \left( t/\tau_2 \right) \quad \text{Eq. (10)}
\]

\[
Q_1 = \frac{\varepsilon_2}{\varepsilon_1} Q_2 \quad \text{Eq. (11)}
\]

The physical significance of the relationship presented in Eq. (9) is that it defines the critical flow rate, \( Q_\text{cr} \), to flow rate of \( Q_a \) and the ratio of efficiency \( \varepsilon_1/\varepsilon_2 \) at which critical flow rate the same particle concentration profile is achieved.
Once slurry is transferred to the CMP slurry distribution system, a portion of the CMP slurry is delivered to the CMP polishers and the excess amount of slurry is recirculated to the day tank. The recirculation of CMP slurry to the day tank keeps slurry in a steady flow condition to minimize stagnation and settling. Figure 3 represents a partial flow recirculation system with two stage filtration.

The mass balance of particle concentration as a function of time, $t$, of the partial flow recirculation system leads to a first order differential equation as follows.

$$\frac{d(VC)}{dt} = QrC - QC \quad \text{eq. (10)}$$

Assuming, constant filtration efficiency $\epsilon_1$ and $\epsilon_2$ and uniform particle concentration, $C$, in the system, then, the normalized particle concentration, $C/C_0$, in the tank of initial volume, $V_0$, would follow the relationship:

$$C/C_0 = e^{-\xi \frac{t}{\tau}} \quad \text{eq. (11)}$$

where

$$\xi = \left(\frac{Qr}{Q_2}\right) \left(\frac{\epsilon_1}{\epsilon_1 + \epsilon_2} - \frac{\epsilon_1 \epsilon_2}{\epsilon_2}\right)$$

$$\tau = \frac{V_0}{Q_2}$$

### Model Computation of Particle Concentration Profiles for a Closed Loop Filtration System

By using equation (5), normalized particle concentration profiles were computed based on single stage efficiency of $\epsilon_1$ and/or $\epsilon_2$ for a batch size of 30 gallons operating under recirculation filtration scheme. In single stage filtration, a filter efficiency of 90% and a flow rate of 1.0 gpm were used in computation. In one of the two-stage filtration schemes, efficiencies of 20% and 90% were used for the pre-filter and final filter, respectively. For the other two-stage filtration scheme, efficiencies of 20% and 80% were used for pre-filter and final filter, respectively. The recirculation flow rate of 1.0 gpm was chosen for the 95% efficient filter and 1.5 gpm for the 80% efficient filter since the latter is a slightly more open filter.

The computation results showed that the two stage filtration with 20% and 80% efficiency achieved the fastest particle reduction for a given filtration time due to the rapid bath turn over rate of 20 minutes. The particle reduction is similar between the single stage filtration with a 90% efficient filter and the two-stage filtration consisting of a 20% efficient pre-filter and 90% efficient final filter because of the slow bath turnover rate of 30 minute.

A recent filtration study\textsuperscript{2} demonstrated that the final filtration governs the effluent quality. The major role of pre-filtration is to capture a portion of oversized particles while protecting the final filter from premature plugging in order to deliver maximum filter service life. It is evident that the bath turnover rate plays a key role in determining effluent quality in a CMP slurry system operating under a closed loop recirculation mode of filtration. Proper filtration with consideration to bath turnover rate and filter efficiency are critical to remove oversized particle from a CMP slurry.

### Figure 3. Schematic of a partial flow recirculation system

### Figure 4. Normalized Particle Concentration Profile of a 30 Gallon Day Tank with Single and Two Stage Closed Loop Filtration

### Model Computation of Particle Concentration Profiles for a Partial Flow Recirculation Filtration System

By using equation (11), normalized particle concentration profiles were computed based on single stage efficiency data for a bath size of 30 gallons operating under partial flow recirculation. In single stage filtration, a filter efficiency of 95% and a recirculation flow rate of 1.0 gpm were used in computation. In one of the two stage filtration schemes, efficiencies of 90% and 95% were used for the pre-filter and final filter, respectively. For the other two stage filtration scheme, efficiencies of 70% and 80% were used for pre-filter and final filter, respectively. The recirculation flow rate of 1.0 gpm was chosen for the 95% efficient filter and 1.5 gpm for the 80% efficient filter since the latter is a slightly more open filter.

The computation results showed that the two stage filtration with 20% and 80% efficiency achieved the fastest particle reduction for a given filtration time due to the rapid bath turn over rate of 20 minutes. The particle reduction is similar between the single stage filtration with a 90% efficient filter and the two-stage filtration consisting of a 20% efficient pre-filter and 90% efficient final filter because of the slow bath turnover rate of 30 minute.
The flow of CMP slurry delivered to the polisher was maintained at a constant rate of 0.1 gpm for all these cases. The resulting particle concentration profile is presented in Figure 5.

The computation results showed that the two stage filtration with 70% and 80% efficiency achieved the fastest particle reduction for a given filtration time due to the high recirculation flow rate. The particle reduction is similar between the single stage filtration with a 95% efficient filter and the two stage filtration consisting of a 90% efficient pre-filter and 95% efficient final filter. Hence, the final filtration governs the effluent quality. The major role of pre-filtration is to capture a portion of oversized particles while protecting the final filter from premature plugging in order to deliver maximum filter service life. It is evident that the recirculation plays a key role in determining effluent quality in a CMP slurry system operating under a partial flow recirculation mode of filtration. Hence, proper filtration with considerations to recirculation flow rate and filter efficiency are critical in removing oversized particles from a partial recirculation flow of a CMP slurry distribution system.

Results and Discussion
In the filtration experiments, single stage, recirculation filtrations were performed under constant pressure to remove oversized particles from colloidal silica based CMP slurry. Table 1 summarizes the particle removal efficiency @ ≥0.54 µm of Betapure™ CMP series filters and some competitive filters with micron ratings ranging from 0.5 to 10 µm.

As expected and presented in Table 1, tighter filtration results in greater reduction of oversized particles from the CMP slurries. The oversized particle removal efficiency @ ≥ 0.54 µm improves with respect to recirculation time at 10, 60, 120, and 180 minutes as shown in Table 1. In this work, particle concentration differential distribution curves were obtained to reveal the full impact of the recirculation filtration on the removal of oversized particle ≥ 0.54 µm. Since filter performance varies greatly from one supplier to the next, Figures 6 to 8 demonstrate the difference in the particle concentration differential distribution curves for three equivalent rated filters including 3M Purification, competitor M, and competitor P, respectively.
Figure 6. Oversized Particle Size Distribution Before and After Betapure™ CMP 570 Filtration

Figure 7. Oversized Particle Size Distribution Before and After Competitive M1050 Filtration

Figure 8. Oversized Particle Size Distribution Before and After Competitive P1 100 Filtration
The objective of a CMP slurry filter is for the majority of desired abrasive particles to pass through it unchanged, while only removing the undesired or oversized particles. If the desired abrasive particles were removed due to over filtration, then the end point of the CMP process cannot be reliably determined and would lead to under polishing and yield loss. The results of percent solids of the influent and effluent samples are summarized in Table 2.

Upon examining the percent solids data presented in Table 2, the percent solids of the effluent samples remain at or near that of the influent samples regardless of filter micron ratings, or effluent sampling points as a function of time. However, the Competitive P1 005 filter is the only exceptional case. As indicated in Table 2, there is a 10% reduction in percent solids for effluent samples after the Competitive P1 005 filtration.

Statistical analysis was performed to determine whether the averaged value of percent solids between the influent and effluent was different. T-test statistics were carried out on the data presented in Table 2. Within the 95% confidence interval, the percent solid of the influent is different from that of the effluent samples for the Competitive P1 005 filter. This indicates that the difference in percent solids for the Competitive P1 005 filter is statistically significant and beyond the uncertainties involved with the Si measurements by using ICP. Therefore, the reduction of 10% percent solids can be partially attributed to the stripping out of some of the desired abrasive particles in the slurry by the Competitive P1 005 filter.

**Comparison of the Predicted and Experimental Particle Concentration Profiles**

To compare the particle concentration profile predicted by the proposed model with the experimental data, Eq. (6) and Eq. (11) can be used. Both models require efficiency data as determined from single stage, single pass filtration, flow rate, and filtration time. However, the efficiency data reported in Table 1 was generated under single stage, re-circulation conditions. Therefore, the reported efficiency data as shown in Table 1 are not suitable for the purpose of model computation. In a recent work, single stage, single pass and two stage, recirculation filtrations were carried out using colloidal based copper CMP slurries. As shown in Figure 9, the proposed recirculation filtration model adequately predicted particle concentration profile when compared to the experimental data.

**Table 2. Summary of the Percent Solids of the Influent and Effluent Samples Collected from Various Filters**

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>Percent Solids of SiO₂</th>
<th>Effluent Collected at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>10 min</td>
<td>60 min</td>
</tr>
<tr>
<td>Betapure™ CMP 520</td>
<td>0.381</td>
<td>NA</td>
</tr>
<tr>
<td>Betapure™ CMP 550</td>
<td>0.355</td>
<td>NA</td>
</tr>
<tr>
<td>Betapure™ CMP 560</td>
<td>0.354</td>
<td>NA</td>
</tr>
<tr>
<td>Betapure™ CMP 570</td>
<td>0.356</td>
<td>NA</td>
</tr>
<tr>
<td>Competitive P1 005</td>
<td>0.370</td>
<td>0.345</td>
</tr>
<tr>
<td>Competitive P1 050</td>
<td>0.376</td>
<td>NA</td>
</tr>
<tr>
<td>Competitive P1 100</td>
<td>0.349</td>
<td>NA</td>
</tr>
<tr>
<td>Competitive P2 050</td>
<td>0.356</td>
<td>NA</td>
</tr>
<tr>
<td>Competitive M1050</td>
<td>0.330</td>
<td>NA</td>
</tr>
<tr>
<td>Competitive M2010</td>
<td>0.356</td>
<td>NA</td>
</tr>
</tbody>
</table>

**Figure 9. Normalized Particle Concentration Profile of a 5 Gallon Day Tank with 5.0 to 1.0 µm Two Stage, Closed Loop Filtration and Flow Rate of 0.5 gpm**
To verify the range of applicability of the proposed models, more work is needed to evaluate how well the proposed models predict the particle concentration profile for CMP applications.

Conclusions
Betapure™ CMP series filters demonstrated excellent performance in removing oversized particles while not altering the percent solids after filtration. It was shown that over filtration resulted in a reduction of the percent solids indicating stripping out of some of the desired abrasive particles from CMP slurry. Therefore, proper filtration is critical to achieving optimal filter performance while maintaining the polishing characteristics of the CMP slurry.

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References