Proper Filtration Removes Large Particles from Copper CMP Slurries

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Abstract
Single stage, single pass and multiple stage, multiple (recirculation) pass filtrations were performed to remove large particles counts from colloidal silica based copper Chemical Mechanical Polishing (CMP) slurries. The role of pre-filtration is to capture a significant amount of large particles and to protect the final filter from premature plugging in order to deliver maximum filter service life. Percent solids of CMP slurry samples were found to remain constant after filtration. A mathematical model has been developed to simulate particle reduction in a CMP slurry distribution system when the filtration system is being operated in a recirculation mode. The model predicts particle concentration as a function of the residence time of particles, the particle removal efficiency of the filter, and filtration time. The model shows that flow rate is the most critical parameter in achieving rapid removal of large particles. Based on examination of the limited data, the recirculation flow model adequately predicts the particle removal efficiency. Ultimately, selection of the optimum filters depends on flow rate, particle removal efficiency of the filter, filtration scheme - single vs. multiple 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 large particles greater than 0.5 µm is typically found in the CMP slurry distribution system. Large 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 large particles affect the level of surface defectivity of a wafer after CMP has been completed. Filtration has been shown to be effective in removing large particles from CMP slurry, resulting in a reduction of micro scratches on the surface of the polished wafer surfaces. Hence, filtration has been incorporated into the CMP process for better yield management during the manufacture of integrated circuits.

This study investigates the effectiveness of several filtration modes on the removal of large particle counts from silica based copper CMP slurries and the consistency of solid 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 on the reduction in large particle concentration were used to evaluate the particle concentration profile predicted by the mathematical model.

Experimental
The silica based copper CMP slurries used in this work were obtained from Ashland Specialty Chemical Company. Slurries were filtered through all polypropylene depth filters with micron ratings of 0.3, 0.5, 0.8, 1.0, 5.0, and 10 µm. Filtration was performed with single stage, single pass and multiple stage, multiple pass (re-circulation) filtration schemes. Influent and effluent samples at different filtration times were collected for particle sizing. Particle size analysis for particles greater than 0.5 µm was performed via Accusizer Model 780A from Particle Sizing Systems.

Model Development And Computation
Figure 1 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.

\[ V \frac{dC}{dt} = Q (C_2 - C) \]  
where  
\[ C_2 = C_1 (1 - \epsilon_2) \]  
\[ C_1 = C (1 - \epsilon_1) \]  
\[ C = C_0 @ t = 0 \]

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 would follow the relationship:

\[ C/C_0 = e^{-\xi (t/\tau)} \]  

Where \( C_0 \) is the initial particle concentration prior to filtration and \( \tau \) is defined as a ratio of tank volume to flow rate. The physical significance of \( \tau \) is that it represents the average residence time of particles in the tank which is often referred to as bath turnover rate.
By using equation 5, normalized particle concentration profiles were computed based on a single stage and two stage recirculation filtration for a batch size of 30 gallons (as shown in figure 2). 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 the pre-filter and final filter, respectively. The flow rate of 1.0 gpm was chosen for the 90% efficient filter and 1.5 gpm for the 80% efficient filter since it is a slightly more open filter.

The computation results showed that 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 scheme consisting of a 20% efficient pre-filter and 90% efficient final filter because of the slower bath turn over rate of 30 minutes. It is evident that bath turn over rate plays a key role in determining effluent quality in a slurry delivery system operating under a closed loop re-circulation mode of filtration. Hence, proper filtration with consideration to bath turnover rate and filter efficiency are critical in removing large particle counts from CMP slurry.

Results and Discussion

Particle Size Distribution for Particles > 0.5 µm Before and After Filtration

In the filtration experiment, single pass and multiple stages, re-circulation filtrations were performed to remove large particle counts from colloidal silica based copper CMP slurries. The slurries were filtered through all polypropylene depth filters with micron ratings of 0.3, 0.5, 0.8, 1.0, 5.0, and 10 µm.

As expected, tighter filtration results in a greater reduction of large particle counts from the CMP slurries. In multiple stage filtration, efficiency of the final filtration stage dictates the final effluent quality, which is comparable to a single stage filter for a given final filter rating. The role of pre-filtration is to capture a significant amount of large particles and to protect the final filter from premature plugging in order to deliver extended filter service life.

Particle Removal Comparison of Model Computation and Experimental Data

From the single stage experiment, the efficiency of 5.0 µm and 1.0 µm rated depth filters at > 0.54 µm was determined to be 75% and 90%, respectively. To simulate the performance of a two stage filtration scheme consisting of a 75% efficient pre-filter and 90% efficient final filter, the normalized particle concentration at > 0.54 µm is computed and presented in Figure 3. When the computed particle concentration is compared with the experimental data at a given filtration time, the model adequately predicts the particle concentration profile with filtration time as shown in Figure 3.

Percent Solids

Percent solids of CMP slurry samples were determined by Inductively Coupled Plasma Spectroscopy (ICP) for silicon (Si) and converted to SiO₂. The relative changes of the percent solids of the effluent samples were determined to be within 4 %, 6%, and 5% of the raw CMP slurry A, B, and C, respectively. The changes are well within the experimental uncertainty for measuring the Si content. Therefore, the tested filters did not alter the percent solids of the CMP effluent.
Figure 3. - Normalized Particle Concentration Profile of a 5 Gallon Day Tank with 5µm to 1 µm Two-Stage Closed Loop Filtration and Flow Rate of 0.5 gpm

Model Computation versus Experimental Data @ > 0.54 µm

Normalized Particle Concentration @ > 0.54 µm

Model Computation; ε₁ = 0.75, ε₂ = 0.90

Experimental

Ashland Copper Slurry A

Normalized Particle Size Distribution

Base CMP slurry; before filtration

10 µm Betapure™ CMP filter; 10 minutes filtration

5 µm Betapure™ CMP filter; 10 minutes filtration

1 µm Betapure™ CMP filter; 10 minutes filtration

5.0 to 1.0 µm two stage Betapure™ CMP filters, three pass filtration (~ 30 minutes)

Diameter (micron)

Ashland Copper Slurry B

Normalized Particle Size Distribution

0.5 µm Competitive Filter Inlet

0.5 µm Betapure™ CMP Filter Inlet

1.0 µm Betapure™ CMP Filter Inlet

0.5 µm Competitive Filter Outlet

1.0 µm Betapure™ CMP Filter Outlet

0.5 µm Betapure™ CMP Filter Outlet

Diameter (µm)
Conclusion

3M Purification Inc. filters showed excellent performance in removing large particles while not altering the percent solids before and after filtration. The proposed model adequately predicts the particle concentration profile with regards to filtration time. The model shows that flow rate or bath turnover rate is the most important parameter in achieving rapid removal of large particles. Ultimately, selection of the proper filtration depends on flow rate, particle removal efficiency of the filter, filtration scheme, and filter service life.

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