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Effects of a Circulation on the Particle Size Distribution of Cabot Semi-Sperse® 12 Slurry using a White Knight PCA300 Pump System

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INTRODUCTION

Slurries, suspensions of fine particles dispersed in a liquid, are often used in semiconductor chip manufacturing to planarize wafer surfaces. The effectiveness of these slurries in achieving a flat surface free of scratches is highly dependent upon the physical properties of the slurry. Perhaps the most important physical properties of the slurry are the average size of the fine or "working" particles in the slurry and the presence of large particles, often referred to as the large particle tail, which can cause scratches.

Delivery systems are often used to supply the slurry to the planarization tools. These systems pressurize the slurry to deliver it to the tools and circulate it to help keep the particles in suspension. Pressurization and circulation are accomplished by various means including a variety of pumps technology. Typically, the slurry passes through the equipment providing the motive force approximately 100 times before it is used to polish wafers, i.e. the slurry is "turned-over" approximately 100 times.

Many slurries are easily damaged by mechanical handling. Damage often takes the form of changes in the size distribution of the slurry particles. This test was performed to determine the effect of circulation with a White Knight PCA300 levitated impeller centrifugal pump system on the size distribution of the particles in the slurry. Semi-Sperse® 12, a suspension of fumed silica particles in dilute potassium hydroxide, was used.

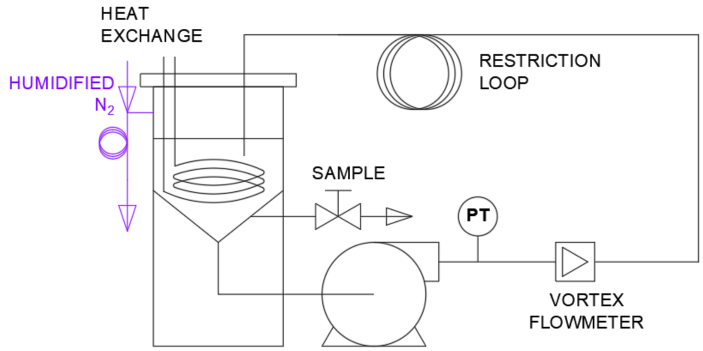
TEST PROCEDURE

The pump was used to circulate 12 liters of slurry at a flow rate of approximately 30 lpm (8.0 gpm) and outlet pressure of 30±5 psig (2.1 bar). Settling of the slurry in the tank was minimized by drawing from the bottom of a conical bottom tank and by turning the volume of slurry in the tank over in less than 30 seconds. The return line to the slurry tank was submerged below the liquid level of the slurry to avoid entraining air into the slurry. The return line was also positioned to minimize the formation of a large vortex in the tank that may entrain air into the slurry. No valves were used to generate back pressure at the outlet of the pump. Instead, long lengths of ½" PFA tubing were used to gradually reduce the pressure from 30 psig at the pump outlet to ambient pressure at the end of the return line to the tank. To achieve these conditions, the pump was operated at 3150 rpm. The slurry was circulated until more than 1,000 tank turnovers were achieved. The test system was constructed of PFA, except for the conical bottom tank that was constructed of polyethylene.

The tank holding the slurry was blanketed with nitrogen to prevent absorption of carbon dioxide from the air, which can change the pH of the slurry. The nitrogen was humidified to prevent dehydration of the slurry. Shifts in the pH and dehydration can both result in particle agglomeration in the slurry. A chiller and stainless steel coil were used to maintain the slurry at 20 ± 2°C during the test. The relative humidity in the tank was > 90% throughout the test.

Samples were drawn from the system at selected times for analysis. The particle size distribution (PSD) was measured using two techniques. The size of the working particles was measured using a Particle Sizing Systems NICOMP 380ZLS, which determines particle size by dynamic light scattering (DLS). The size distribution of the large particle tail was measured using a Particle Sizing Systems AccuSizer 780 optical particle counter (OPC).

Figure 1. – Recirculation Apparatus Schematic



The measurements made using the NICOMP 380ZLS were performed at 23°C on samples of slurry that were diluted approximately 40:1 into deionized water. Each sample was measured for 10 minutes. Triplicate measurements of each sample were made. The size measurement data were analyzed using the instruments Gaussian distribution assumption.

The size distribution of the large particle tail of the slurry was measured with an AccuSizer 780A. This instrument uses a combination of light scattering and light extinction to measure the size distribution of particles > 0.56 µm. The size measurements were performed by diluting the slurry sample by a factor of about 1150:1 into deionized water. Between samples, the entire system was thoroughly flushed with deionized water. Data from selected particle size channels were analyzed.

RESULTS

Figures 2 shows the initial size distributions of the working particles measured using the dynamic light scattering instrument. Both the cumulative and differential distributions are presented. The volume-weighted mean and 99th percentile particle diameters (99% of the particles have diameters less than this size) are also included. Figure 3 shows the initial size distribution of the large particle tail measured by the OPC. Due to variations in starting concentrations, these concentrations will be used as the initial concentration (C_I) used to find the relative concentrations for the remainder of the test.

Figure 2. Initial working particle size distribution

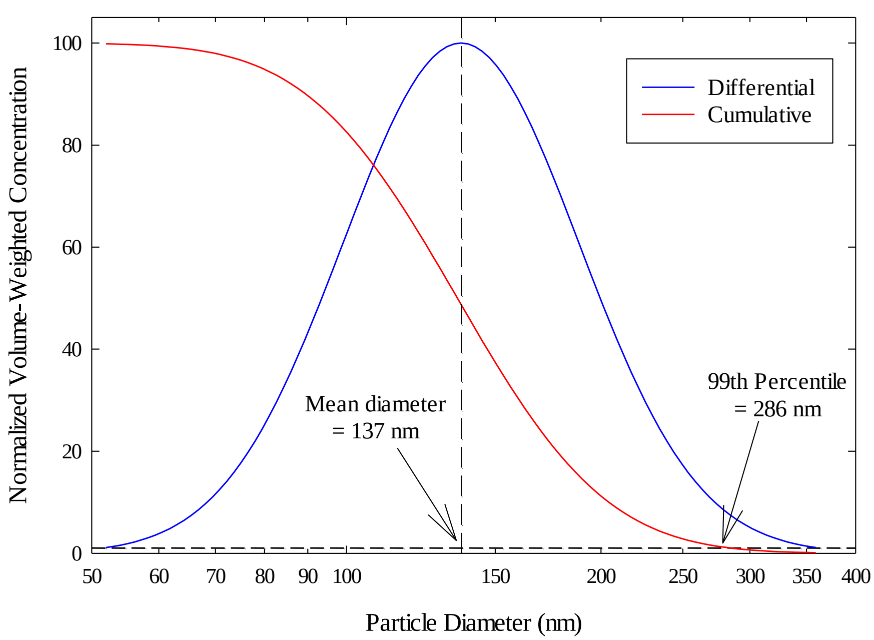


Figure 3. Initial size distribution of the large particle tail

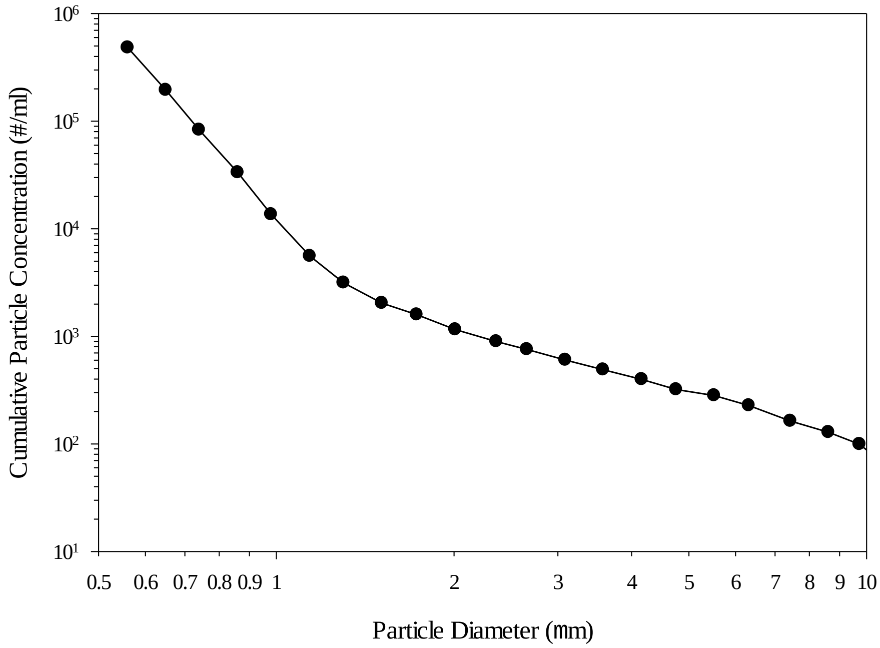
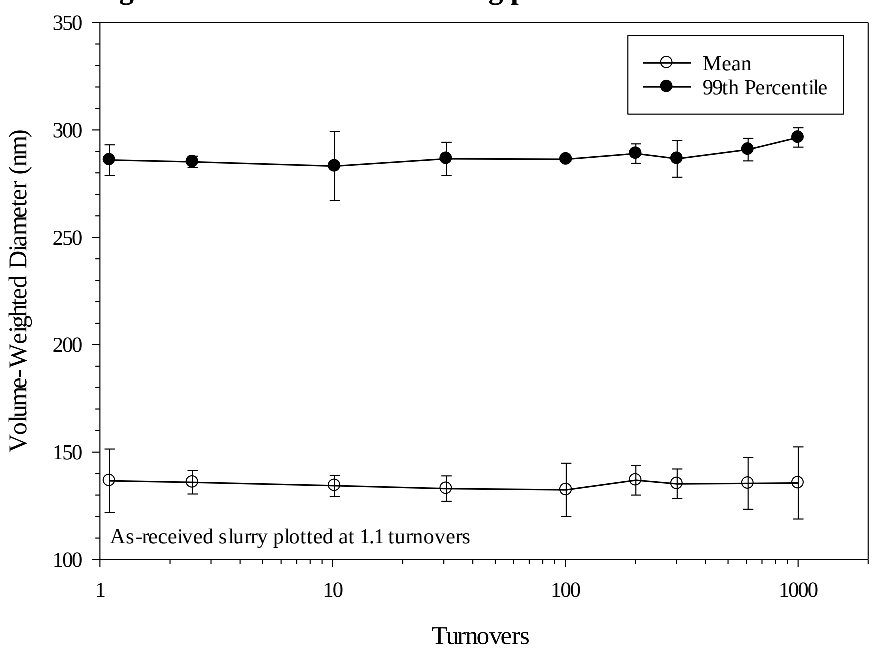


Figure 4 shows the volume-weighted mean and 99th percentile particle diameters of the working PSD as a function of tank turnovers. Error bars are included in the figure and represent ± 3 standard deviations. 99th percentile measurements were observed to increase approximately 3% between 300 and 1000 turnovers. However, no significant change in the mean working particle size was observed.

Figure 4. Effects on the working particle size distribution



Figures 5 presents the ratios of the cumulative particle concentrations at different tank turnovers (C_T) relative to the initial particle concentrations (C_I) for 5 different size channels in the large particle tail, as measured by the AccuSizer OPC. Particles ≥ 0.56 and ≥ 1.0 µm showed minor deviation, if any, during the course of the test. Particles ≥ 2.0 µm showed a stable deviation trend, decreasing to a ratio of 0.6 (C_T/C_I) at the end of the test. Particles ≥ 5.0 µm and ≥ 10 µm exhibited very low counting statistics, resulting in measurement variability, but ultimately show no stable deviation away from initial concentrations. A summary of these results is presented in Table II.

Figure 5. Effects on large particles

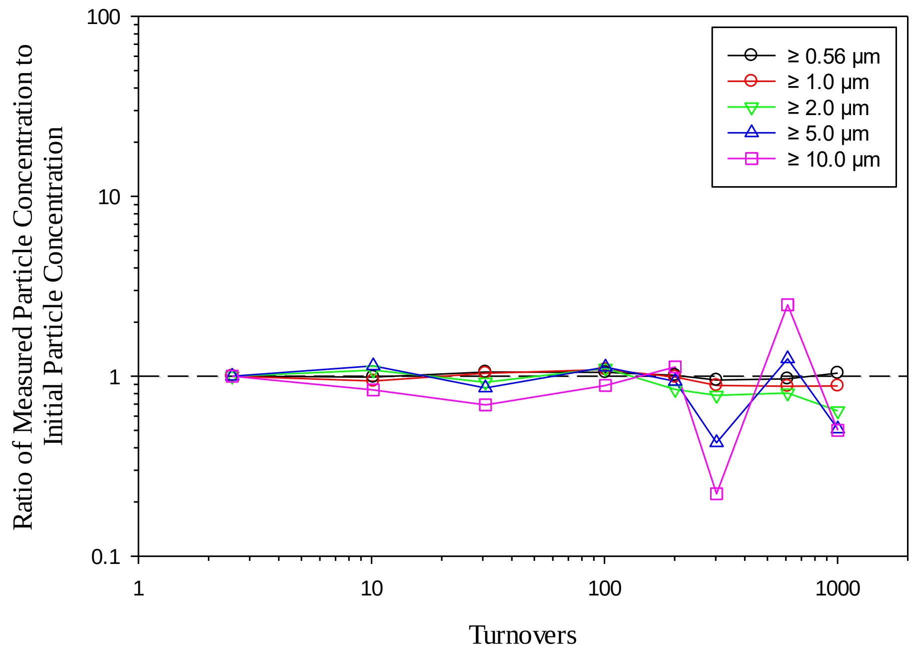


Table II. Particle Concentrations Relative to Initial Concentrations (C_T/C_I)

	Turnovers	
Particle Size	100	1000
≥ 0.56 µm	1.1	1.0
≥ 1.0 µm	1.1	0.9
≥ 2.0 µm	1.1	0.6
≥ 5.0 µm	1.1	0.5
≥ 10 µm	0.9	0.5

Particle agglomeration has been shown to occur in Semi-Sperse® 12 when it is subjected to handling. In previous evaluations, large particle agglomeration of Semi-Sperse® 12, circulated by diaphragm pumps, has been observed [1, 2]. In these previous tests, the concentrations of particles in the large particle tail were found to increase significantly after less than 100 turnovers. No such trends were observed in with this pump system in the scope of this test.

SUMMARY

A White Knight PCA300 centrifugal pump system was tested to determine how its use affects the size distribution of particles in Semi-Sperse® 12 slurry. The slurry was circulated until it passed through the pump approximately 1,000 times.

After 1,000 turnovers, no change in the mean working particle size distribution was observed with DLS. 99th percentile particle size was observed to increase approximately 3% with this measurement method. However, direct measurements of the large particle tail via OPC showed no significant change for particles ≥ 0.56 and 1.0 µm. Particles ≥ 2.0 µm were actually observed to decrease in concentration by approximately 40%. Particles ≥ 5.0 and 10 µm exhibited very low counting statistics, resulting in high measurement variability, and ultimately showed no stable increasing or decreasing deviation trends.

References

1. Nicholes K, R Singh, D Grant, and M Litchy (2001). "Measuring particles in CMP Slurries," Semiconductor International, 24(8): 201-206.
2. Litchy MR, K Nicholes, DC Grant, and RK Singh (2001). "Perturbation Detection Analysis: A method for comparing instruments that measure CMP slurry health," Proceedings of the 19th Annual Semiconductor Pure Water and Chemicals Conference, Sponsored by Balazs Analytical Laboratory, Sunnyvale, pp 153-171.