A NEW METHOD FOR DETERMINING THE SIZE DISTRIBUTION OF PARTICLES IN CMP SLURRIES

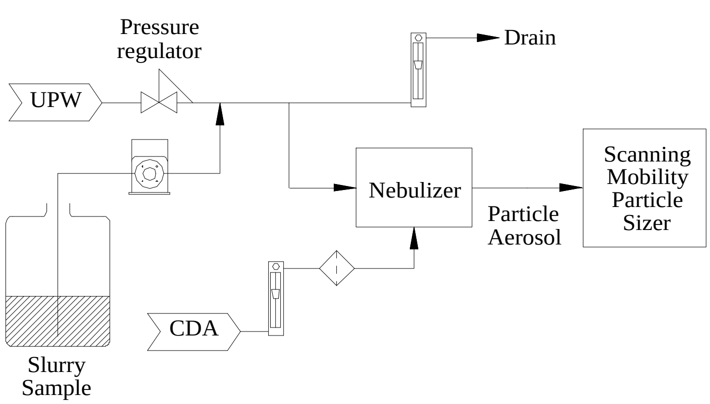
Gary Van Schooneveld, Mark R. Litchy and Donald C. Grant
CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344, U.S.A.
gary@ctassociatesinc.com, mark@ctassociatesinc.com, don@ctassociatesinc.com

The particle size distribution (PSD) of the “working” particles in CMP slurries strongly influences the efficacy of the planarization process. The techniques presently used to determine the PSD typically only measure relative particle concentrations and often presume the shape of the distribution. A new approach uniquely combining proven techniques used for counting and sizing aerosol PSDs has been developed to measure both particle size and number concentration in highly concentrated liquid suspensions. This paper provides a brief description of the new measurement method along with particle data from a number of production slurries using this method.

MEASUREMENT METHOD DESCRIPTION

The measurement system consists of a nebulizer and a scanning mobility particle sizer (SMPS) (Figure 1). A slurry sample is diluted in-line in ultrapure water (UPW) and then injected into the nebulizer. The nebulizer generates a droplet distribution in filtered air. The resultant droplet distribution is diluted and dried with additional filtered air to form an aerosol. The aerosol PSD is then measured using an SMPS system capable of measuring particles as small as 3 nm in diameter. A TSI Model 3936 SMPS was used to generate the data provided.

Figure 1. Schematic of slurry PSD measurement system



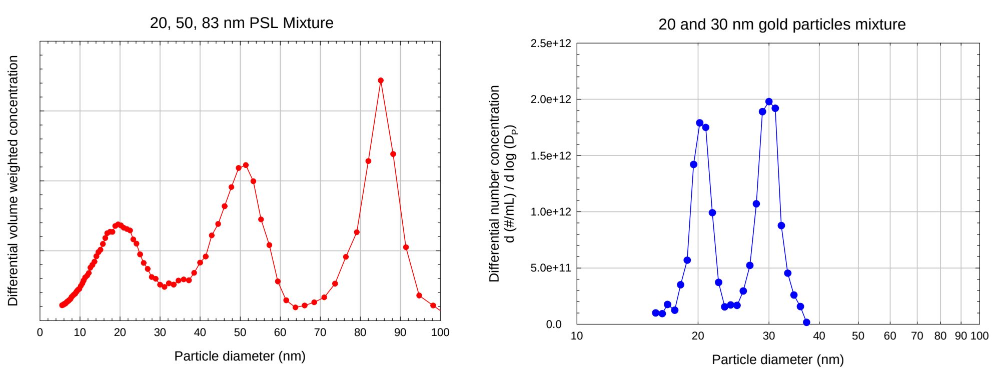
The key to this measurement approach is the nebulizer. Non-volatile dissolved residue in the slurry will form particles when the droplets from the nebulizer are dried. These residue particles can interfere with the slurry particle analysis and increase the lower detection limit of test method. The nebulizer used in this system minimizes this effect by producing droplets that are sufficiently small and uniformly sized that particles formed from dissolved materials in the droplets are so small that they do not interfere with the particle size measurement. CMP slurry samples are often measured at multiple dilution ratios to insure the separation of the soluble and insoluble (particles) non-volatile residue. In addition, the particle suspension is sufficiently dilute such that no more than one particle is present in each droplet.

This technique of measuring CMP slurry PSDs offers many unique advantages over dynamic light scattering, laser diffraction, and other traditional CMP particle sizing methods. Unlike many other methods, no assumption is made regarding the shape of the PSD with this technique. Furthermore, this technique measures actual number concentrations, not relative particle concentrations (that is, concentration of particles of one size relative to concentrations of another size) like other “working” particle sizing techniques. Instruments that provide relative PSDs can lead to significant misinterpretation when comparing different samples because they only provide measurements of relative concentrations within each sample. This measurement method also directly measures number-weighted PSDs, which may be easily converted to alternative weightings such diameter (D), surface area (D^2), or volume (D^3) weighted distributions. Many other techniques measure intensity-weighted (D^6) PSDs which must be converted to another weighting that is physically applicable to the process. This conversion can lead to substantial uncertainties in the resultant number or volume-weighted PSDs. Since this technique measures individual slurry particles, it is highly sensitive to measuring rather small changes in these suspensions. Since the particle size measurement is based on particle electrical mobility, these measurements are independent of the optical properties and density of the particles. The SMPS measurement technique is a proven technique for measuring aerosol PSDs in the aerosol measurement community for more than two decades (1) and is used to measure particle size standards by NIST (2).

TEST RESULTS

The sizing accuracy of the nebulizer-SMPS (N-SMPS) measurement system is shown in Figure 2. In the left graph, the result of a three-size polystyrene latex particle mixture is shown. In right graph, a combined solution of gold particles was measured. The sizing results correlate well with the manufacturer’s sizing and standard deviation data.

Figure 2. Measurement of standard particles using the N-SMPS system



The results from the N-SMPS used to measure a multi-modal colloidal silica slurry are presented in Figure 3. As discussed previously, the N-SMPS directly measures particle concentration of the slurry. Assuming that the particles measured are spherical, diameter, area and volume-weighted distribution can easily be calculated from the number concentrations. Using the number-weighted distribution allows for good resolution of the small particle portion of the distribution while the volume-weighted distribution provides better detail for the larger particle sizes.

The potential advantages of directly measuring the number and size of the slurry particles and not having to assume a particle size distribution are seen in Figure 4. In this evaluation, factory-fresh colloidal slurry is compared to reclaimed and reprocessed slurry using three techniques; dynamic light scatter (DLS), laser diffraction (LD) and nebulizer-SMPS. The data from the dynamic light scattering and laser diffraction instrument do not show a significant difference between the two slurries. In addition, there is limited, if any, data provided concerning the modality of the slurry. Meanwhile, the nebulizer-SMPS system clearly shows that the slurry is tri-modal. In addition, the method detected a non-uniform increase in the particle concentration between the reclaimed slurry compared to the factory fresh slurry with the concentration of small particles (10-50 nm) increasing more than the concentration of the large particles (80-400 nm). An overall increase in concentration for the reclaimed slurry was later revealed to be consistent with the reprocessing method used, but the non-uniformity was not expected.

Figure 3. Example of a tri-modal colloidal silica slurry using the N-SMPS system

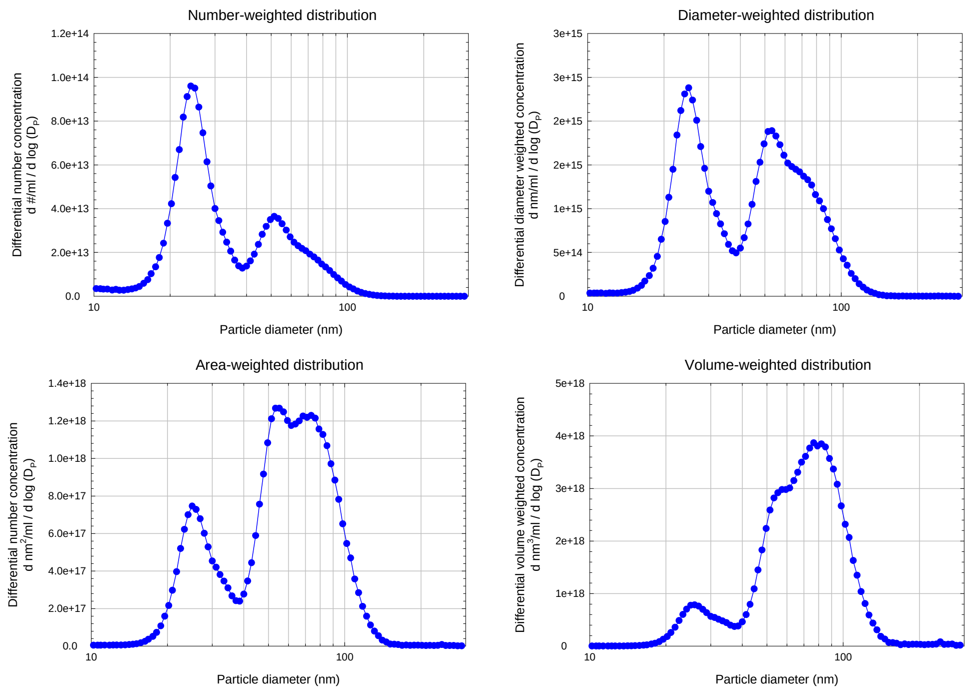
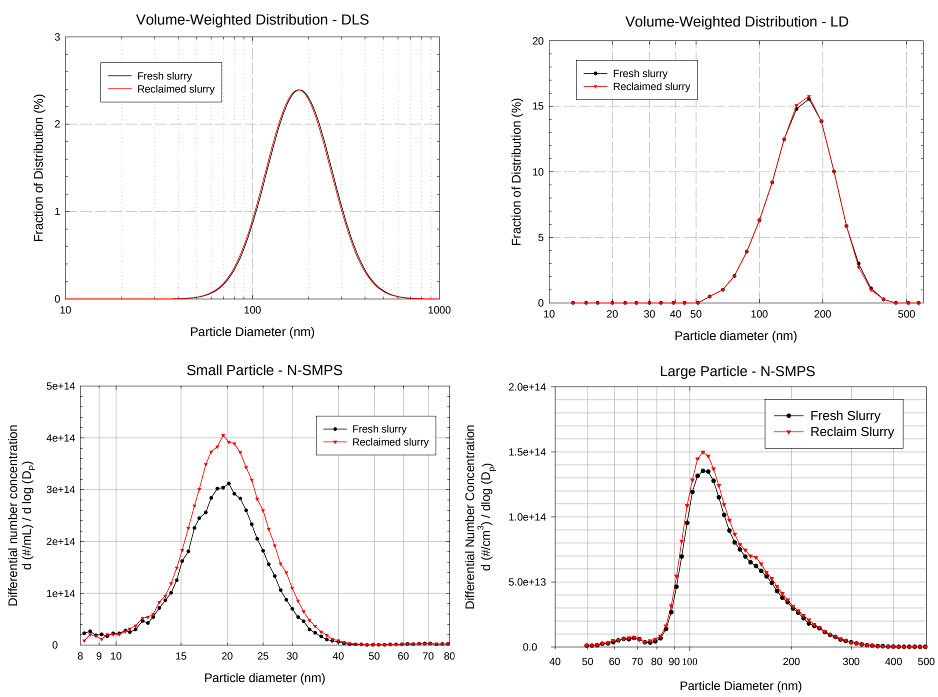


Figure 4. Three technique comparison of new and reclaimed colloidal silica slurry



The ability to directly measuring particle concentration of slurry allows for detecting potential cross-contamination of slurries. Figure 5 shows the effect of adding a small amount of silica slurry to alumina slurry. Establishing “cross-contamination finger-prints” such as these could be useful in detecting cross-contamination events that might occur in the fab or at the slurry manufacturer.

It is well established that handling of slurry can result in changes in the particle size distribution and agglomeration of slurry particles (3). Figure 6 shows the cumulative effect of circulating a batch of colloidal silica slurry. As the number of turn-overs (passes through the pumping system) increase, the concentration of small particles decreases (left graph) and the number of large particles increases (right graph). These data would suggest that this slurry is susceptible to handling damage with small particle agglomerating to form large particles.

Figure 5. Cross-contamination detection of an alumina/colloidal silica mixture

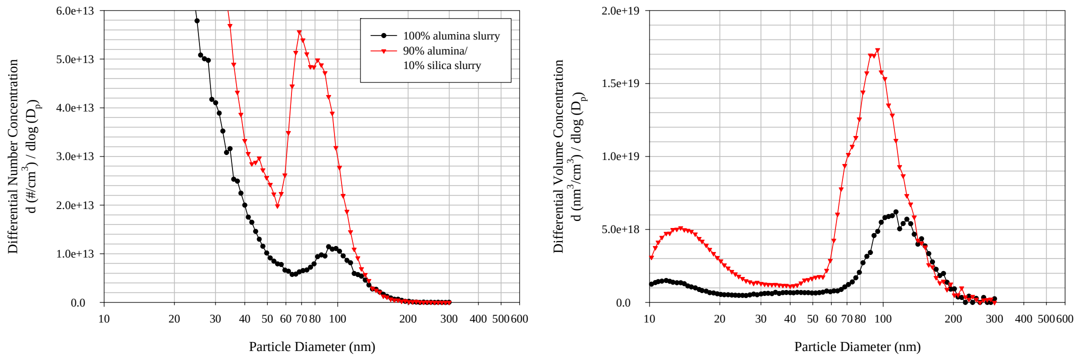
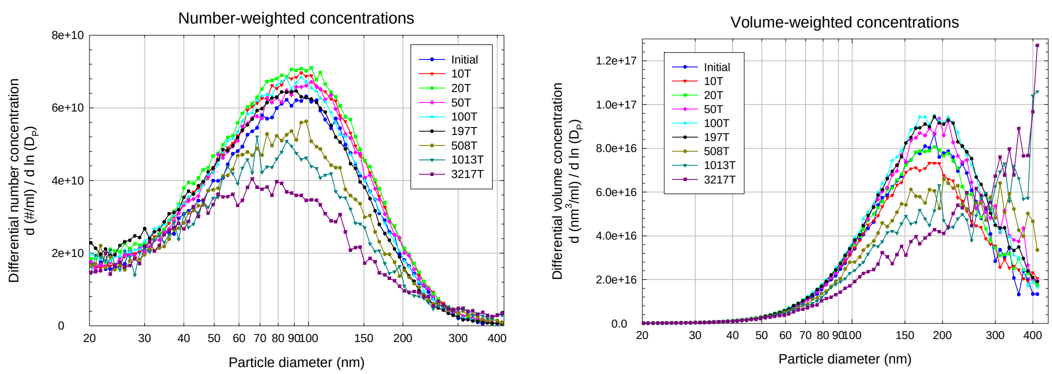


Figure 6. Example of changes in the PSD measured during circulation of a colloidal silica slurry



SUMMARY

A new test method has been developed that provides the ability to directly measure number-weighted size distributions of particles in CMP slurries. Since the method directly measures particle concentrations and can detect particle sizes down to 3 nm, detailed information concerning the small slurry particles (< 50 nm) can be accurately determined and small differences in concentrations for all particle sizes between slurry samples can be identified.

REFERENCES

1. Wang SC and RC Flagan (1989). "Scanning Electrical Mobility Spectrometer," Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, pp. 138-178.

2. Donnelly, MK and Mulholland (2003). "Particle size Measurement for Spheres with Diameters of 50 to 400 nm", National Institute of Standards and Technology, Report # NISTIR 6935.

3. Litchy MR and DC Grant (2007). "Effect of Pump Type on the health of various CMP slurries", *Semiconductor Fabtech*, 33rd Edition, pp 53-59.