Mean Particle Size and Zeta Potential Analysis of CMP Slurries

Nicomp® DLS system

Chemical mechanical polishing/planarization (CMP) is a process widely used in the microelectronics industry to smooth surfaces with the combination of chemical and mechanical forces. This process uses an abrasive and corrosive slurry to help planarize the wafer surface. The CMP slurry is a complex mix of nano-sized abrasive particles and other chemicals including surfactants, pH adjusters, oxidizers, organic acids, and complexing agents. The particle size distribution of the abrasive is a critical parameter affecting the overall process in several ways. The mean size of the abrasive impacts the material removal rate (MRR) with some data and models suggesting a direct relationship, while others suggest an inverse relationship.[1,2] The width of the distribution is also important, again in a complex fashion with both a size dependent and number dependent region having opposite effects on MRR.[2] The presence of large particle counts (LPCs) can have a deleterious effect on yield by causing scratches and defects.[3,4] The surface charge (zeta potential) of the abrasive particles influences dispersion stability and affinity of particles to wafer surfaces.[5]

A variety of abrasive suspensions used in CMP slurries were analyzed using the Nicomp® dynamic light scattering (DLS) system to determine mean size, width of distribution, and zeta potential. The Nicomp system (Figure 1) used for these studies was equipped with a 35 mW 658 nm laser and two detectors; a high gain avalanche photodiode (APD) for particle size and a photomultiplier tube (PMT) for zeta potential. This instrument included a multi-angle goniometer, capable of measuring particle size across a wide range of angles.

Figure 1. Nicomp DLS system.

DILUTION EFFECTS

Most sample preparation investigations when using DLS begin by determining the effect of dilution.[6] All abrasives in this study are too concentrated to measure without dilution, even when correcting for viscosity. This point is made clear in Figure 2 showing the raw data correlation function for a ceria abrasive diluted 2:1. As seen in Figure 2, there is no curve to fit, just a straight line, indicative of either no particle motion or no light scattering from Brownian motion arriving at the detector.

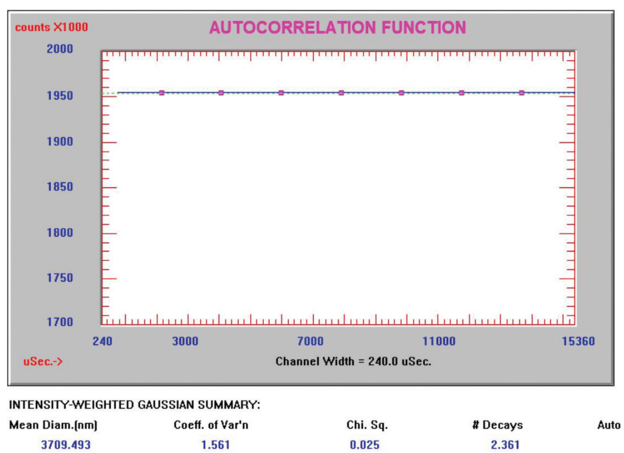

Figure 2. Ceria abrasive correlation function diluted 2:1.

Knowing that dilution is required, the next step is to determine the proper dilution ratio. Even when correcting for viscosity it is suggested to check for errors due to either multiple scattering or restricted diffusion. Both mechanisms add unknown errors to the final calculated results. Multiple scattering occurs when the scattered light from a diffusing particle interacts with one or more additional particles before arriving at the detector. Multiple scattering is suspected when the mean size increases and the width of the distribution (polydispersity index, or PI) decreases with dilution. Restricted diffusion occurs when the translational diffusion is hindered by the presence of nearby particles. Restricted diffusion is suspected when the mean size decreases with dilution while little change is reported in width of the distribution, or PI.

A dilution study of an alumina-based abrasive was performed using the Nicomp system across a range of dilution ratios. For example, 100 µL of sample was diluted into 99.9 mL of DI water and is noted as D1000. Figure 3 shows that the results were fairly stable across the range of dilutions, but size and PI increased at higher concentrations.

Dilution	Size	PI
D1000	98.9 nm	0.086
D250	99 nm	0.089
D125	99.1 nm	0.099
D62.5	99.3 nm	0.092
D31.25	99.3 nm	0.087
D15.6	99.6 nm	0.096
D7.8	99.5 nm	0.094

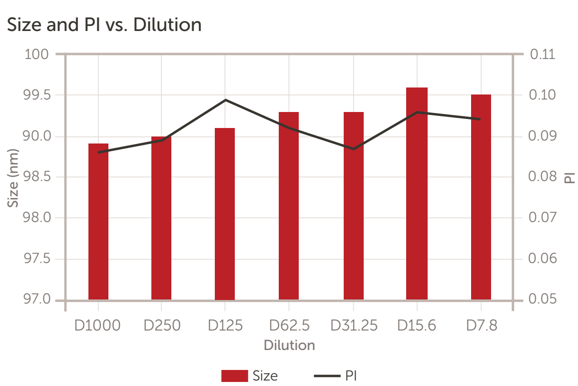

Figure 3. Alumina dilution study. Tabular and graphical results. Lower: size (left Y axis) and PI (right Y axis).

While this study may be instructive for pointing out the effect of restricted diffusion many analysts may decide all results are close enough that any of these dilution ratios are acceptable.

A dilution study of a ceria-based abrasive provided evidence of multiple scattering influencing results. For this sample the reported mean size decreased at higher concentrations while the PI increased, as seen in Figure 4.

Dilution	Size	PI
D1000	133 nm	0.112
D100	131.1 nm	0.111
D10	122.9 nm	0.176
D5	114.2 nm	0.181

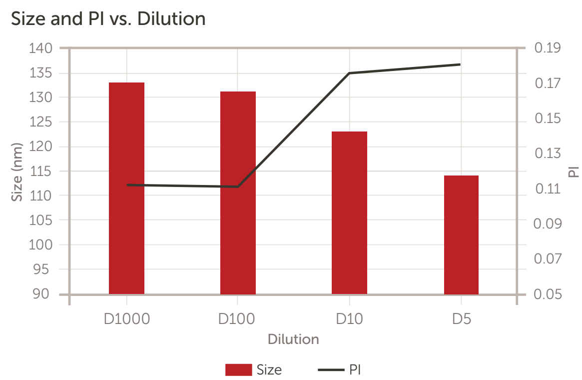

Figure 4. Ceria dilution study. Tabular and graphical results. Lower: size (left Y axis) and PI (right Y axis).

DISTRIBUTION WIDTH

The width of the abrasive particle size distribution (PI) also affects the MRR as mentioned above.[2] Two colloidal silica abrasives were analyzed on the Nicomp system. The smaller size abrasive has a much wider distribution than the larger size abrasive with a narrower distribution. Results in Figure 5 show the great difference in width of particle size distribution.

Sample	Mean	PI
Narrow	80.9 nm	0.008
Wide	20.1 nm	0.325

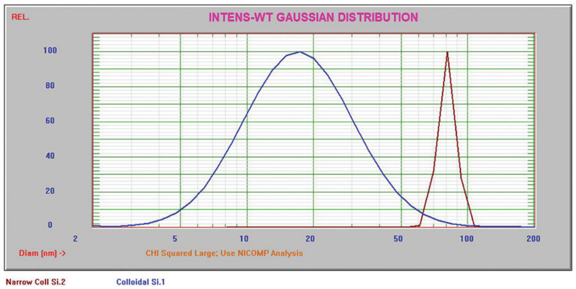

Figure 5. Width of distribution difference in two silica abrasives.

MONOMODAL VS. MULTIMODAL

Two algorithms are used in the Nicomp system[7] to convert the correlation function into a particle size distribution – Gaussian (monomodal) and Nicomp (multimodal). Figure 6 shows the Nicomp system bimodal result for a colloidal silica. The manufacturer's specification sheet for this abrasive reports a primary and secondary peak close to the sizes in the range seen here.

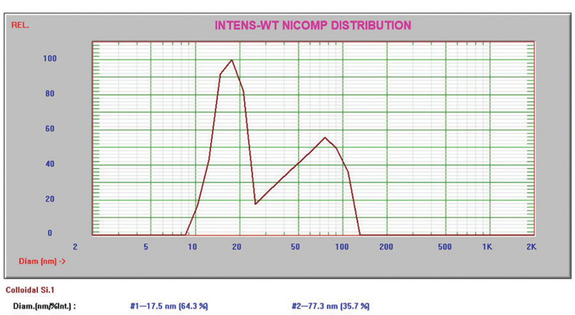

Figure 6. Bimodal colloidal silica abrasive.

RANGE OF SIZES

The dynamic range of DLS is approximately 1 nm to 1+ μm (system and sample dependent). This dynamic range is well suited to determine the mean size of the vast majority of abrasives used for CMP slurries. Figure 7 shows the wide range of reported particle size distributions for four kinds of abrasives; colloidal silica, alumina, ceria, and fumed silica.

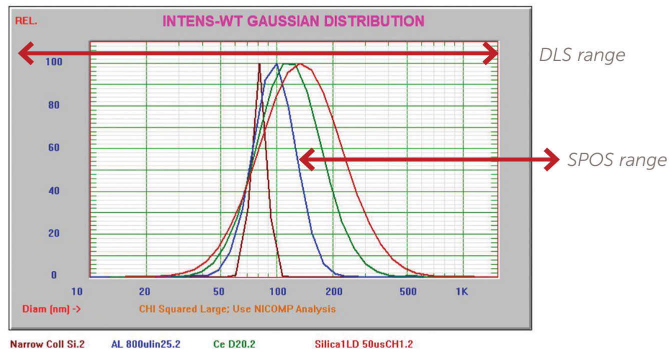

Figure 7. Range of size distributions for various abrasives.

LARGE PARTICLE COUNTS

While DLS is the preferred technique for determining the mean size of submicron abrasive slurries, this technique is not the best way to measure LPCs. DLS and other ensemble light scattering techniques such as laser diffraction can calculate multimodal distributions but lack the resolution to detect a small number of particles at the tails of the distribution. LPCs are typically monitored by liquid particle counters using the technique of single particle optical sizing (SPOS) that provide the additional benefit of concentration data in particles/mL. The AccuSizer® lab and Mini online SPOS systems have proven to be the most sensitive and accurate technique for LPCs.[8–12] The distribution ranges seen in Figure 8 help explain one of the reasons why there are multiple AccuSizer Mini systems for tracking LPC tails. Different size ranges, concentration limits, and dilution fluidics are required to optimize the measurement for a wide variety of abrasive types.

ZETA POTENTIAL

Submicron suspensions like these abrasives are often electrostatically stabilized in order to control the size distribution and shelf life of the product.[13] By increasing the charge on the surface of the particles they repel each other like magnets and never get close enough to agglomerate. It does not matter if the particles are positively or negatively charged, only the absolute magnitude is important. Several abrasive types can be formulated to possess either negative or positive charge depending on the chemistries used.

Two alumina abrasives were analyzed by the Nicomp system to determine the zeta potential. The results in Figures 8 and 9 show one negatively and one positively charged suspension.

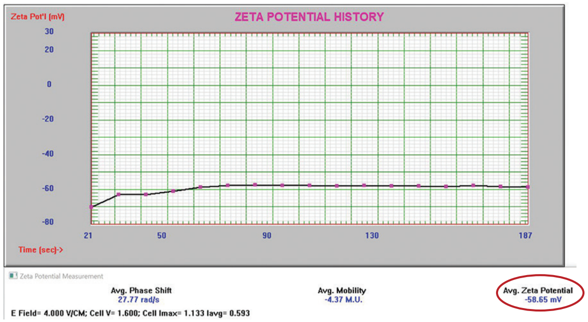

Figure 8. Negatively charged alumina abrasive zeta potential.

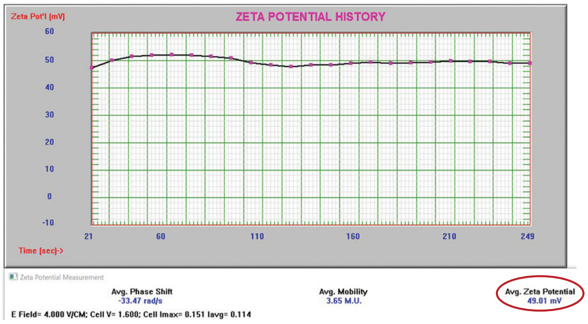

Figure 9. Positively charged alumina abrasive zeta potential.

Another important consideration is to avoid the pH where the zeta potential equals zero, known as the isoelectric point,[14] or IEP. The positively charged alumina slurry shown in Figure 9 was titrated from positive to negative charge to determine the IEP. The pH was altered using 0.1 M KOH titrating from lower to higher pH. The results are shown in Figure 10.

pH	Zeta potential
7.75	36.97
8.27	30.84
8.52	25.9
9.08	14.1
9.46	-1.72
10	-22.49

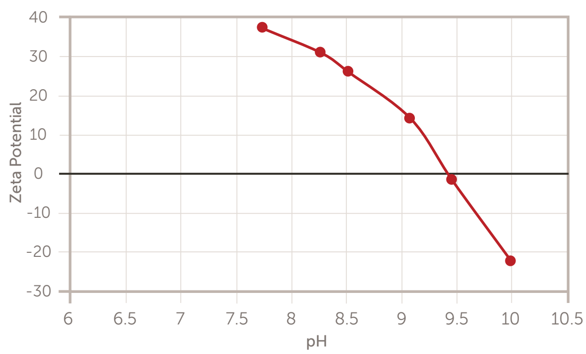

Figure 10. IEP titration of alumina slurry.

The particle size increased dramatically from a mean of 78.4 nm to 3735.6 nm after passing through the IEP at pH 9.4. This is expected because the particles tend to agglomerate in the absence of a charge less than about 10 mV.

CONCLUSIONS

Dynamic light scattering is the preferred method for particle size and zeta potential analysis of abrasives used for CMP slurries. Proper sample preparation is important to generate the most accurate and repeatable results. The Nicomp DLS system is well suited for making the mean size and zeta potential measurements of submicron abrasives. The AccuSizer SPOS is the preferred technique for determining LPC tails in abrasives and final CMP slurries.

References

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[4] Kim S.-K. et al, *Effect of calcination time on the physical properties of synthesized ceria particles for the shallow trench isolation chemical mechanical planarization process*, Journal of Ceramic Processing Research, Vol. 7, No. 1, pp. 53-57 (2006)

[5] Sorooshian, A., et al., *Effect of Particle Interaction on Agglomeration of Silica-Based CMP Slurries*, MRS Proceedings, Vol. 816, 2004

[6] Entegris Technical Note – *DLS Sample Preparation*

[7] Entegris Technical Note – *DLS Data Interpretation*

[8] Entegris Application Note – *Detecting Tails in CMP Slurries*

[9] Entegris Application Note – *SPOS vs. Laser Diffraction*

[10] Entegris Application Note – *Ceria CMP Slurry Monitoring*

[11] Entegris Application Note – *Detecting Tails in CMP Slurries*

[12] Entegris Application Note – *CMP Slurry Filter Testing*

[13] Entegris Application Note – *Dispersion Stability*

[14] Entegris Application Note – *Isoelectric Point (IEP) Determination*

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