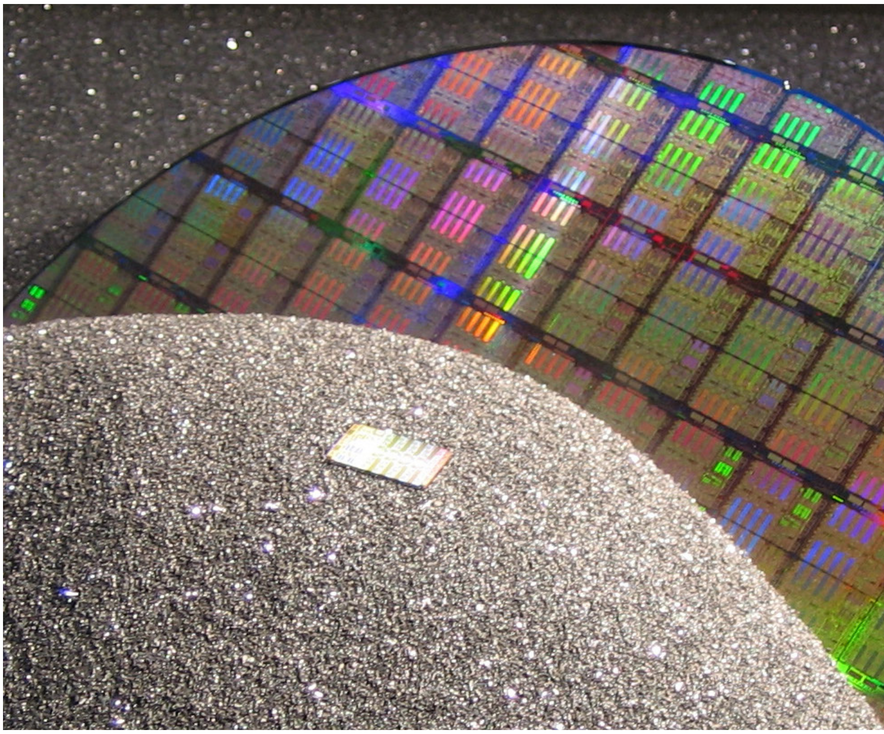

APPLICATION NOTE

ICP-Mass Spectrometry

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Analysis of CeO_2 Chemical Mechanical Planarization Slurries Using SP-ICP-MS

Introduction

Chemical mechanical planarization (CMP) is a process for polishing wafer surfaces used in semiconductor manufacturing. It uses a slurry containing both nanoparticles and functional chemicals. Cerium dioxide (CeO_2) particles are commonly used in CMP slurries, and the sizes of the particles in the slurry are extremely important. Particles in the working (or average) size range remove the target material, but larger particles outside the working size range can scratch or gouge the wafer surface, leading to mechanical damage which reduces semiconductor manufacture yield. Since it only takes a small number of larger particles to cause damage, it is very important to characterize CMP slurry mixtures and abrasive raw materials prior to use to determine the large particle count or concentration (LPC). LPC results can be used to compare why some slurry samples cause more defects than others and which abrasive raw material lots are more preferable for CMP use. This level of detail on the particle size distribution is also critical for abrasive manufacturing, so processes that decrease LPCs can be optimized and refinement techniques to remove LPCs can be accurately compared.

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Ensuring product quality drives the quest for robust techniques for LPC determination. One of the challenges to nanoparticle metrology is being able to find and quantify these larger particles that exist in small numbers relative to the abundant particles in the working range. Traditional particle analysis metrology that uses laser diffraction or light scattering to characterize size distributions has difficulty detecting small concentrations of particles outside the size range of the majority because their relatively small signal is drowned out by the larger signal. As a result, these techniques are geared toward detection of an average size rather than analysis of individual outlier particles. Therefore, they are not always effective in finding the few larger, defect-causing, particles in CMP slurries.

Laser/light-based particle sizing techniques are further limited in that they are bulk property measurements that cannot differentiate between types of particles and may be influenced by other components in the slurry that may also scatter light, such as polymers and surfactants. Results from light-scattering-based particle sizing techniques also typically represent the hydrodynamic particle size, which is larger than the actual solid particle size and may be affected by organic components on the surface of the particle or by changes in dilution techniques during sample preparation.

A solution to these limitations is single particle ICP-MS (SP-ICP-MS), a technique which is capable of determining low concentrations of particles in much shorter times than traditional particle analysis techniques[1,2]. In addition, SP-ICP-MS is selective to specified metallic types of particles, so size results are not affected by chemical components in the slurry or particles of other elemental composition. Initial studies have shown that SP-ICP-MS is effective in CMP slurry analysis[3]; this work expands upon the initial studies by exploring its use to quantify LPCs in addition to the mean particle size (MPS).

Experimental

Samples and Sample Preparation

Three lots of ceria-based CMP slurries were measured. Sample preparation involved sonicating and diluting the slurries with deionized water until particle concentrations were approximately 100,000 particles/mL (part/mL). Diluted samples were sonicated again prior to analysis.

Instrumentation and Measurement

All measurements were made with a PerkinElmer NexION® ICP-MS using the Syngistix™ Nano Application Software Module for all data acquisition and processing. The instrumental conditions and method parameters are shown in Table 1. The transport efficiency was determined by aspirating 60 nm gold nanoparticles at a concentration of 100,000 particles/mL, while dissolved calibrations were carried out with 1, 2, and 3 µg/L cerium (Ce) standards. Because only Ce is being detected by ICP-MS (rather than the whole CeO_2 particle), it is important to enter the mass fraction of Ce (81.40%), as well as the density of CeO_2, in the Nano Application Module for correct calculation of particle size.

Table 1. NexION ICP-MS Instrumentation and Method Conditions.

Parameter	Value
Sample Uptake	348 µL/min
Nebulizer	Glass concentric
Spray Chamber	Glass cyclonic
Nebulizer Flow	Optimized for maximum sensitivity
RF Power	1600 W
Analyte	Ce 140
Density	7.65 g/cm^3
Mass Fraction	81.40%
Analysis Mode	Standard
Dwell Time	50 µs
Analysis Time	120 sec
Transport Efficiency	7.29%

Results and Discussion

A typical size distribution histogram of a CMP slurry (monitoring Ce^+) is shown in Figure 1. This plot shows that the most frequent size is 20 nm, although, peaks at 30, 40, and 50 nm are also present, displaying a fairly broad particle size distribution. Not shown in this figure are particles larger than 60 nm, although they were detected. This type of information allows for the determination of both the size and distribution of the particles present, as well as the concentration of each particle size or in a specific range.

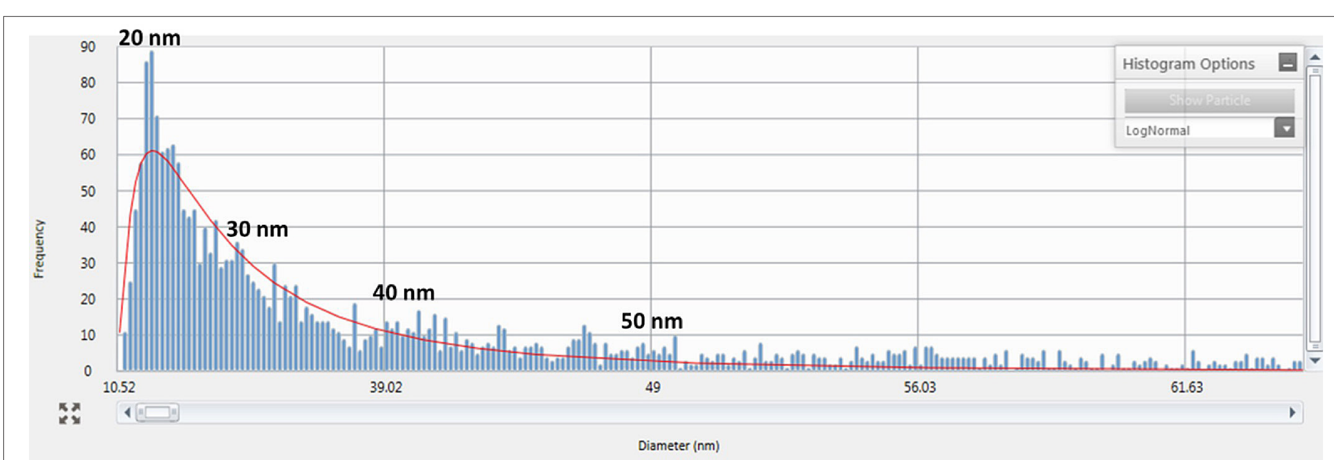

Figure 1. Histogram showing particle size distribution of a typical CMP slurry.

The particle size and concentration for three lots of ceria-based CMP slurries are shown in Table 2. These results indicate that Sample 1 has a mean particle size (MPS) 10 nm (20%) larger than Samples 2 and 3. Because SP-ICP-MS counts individual particles, particle concentrations can also be determined for specific size fractions of interest. The LPC can be determined by counting particles above a specific threshold. In these slurry samples, particles greater than 100 nm and 150 nm have been selected to represent the LPC threshold. Along with the change in MPS, Sample 1 also had a higher LPC at the 100 nm cutoff by about 40%, and twice as many particles at the 150 nm cutoff. The ability to quickly determine particle size in CMP slurries is important so that samples can be screened prior to use. Here, Sample 1 clearly has a higher concentration of larger particles than Samples 2 and 3 and may cause a higher level of scratch defects during CMP processes.

Conclusion

This work has demonstrated the ability of SP-ICP-MS to rapidly determine CeO_2 particle sizes and concentrations in CMP slurry mixtures. Counts at specific size thresholds enable a novel way of quantifying large particles at the tail end of the particle-size distribution. This information allows CMP slurry developers to anticipate performance differences in their slurries prior to use.

References

1. Stephan, C., Neubauer, K. "Single Particle Inductively Coupled Plasma Mass Spectrometry: Understanding How and Why", PerkinElmer white paper, 2014.
2. Hineman, A., Stephan, C. JAAS, 2014, 29, p. 1252.
3. Davidowski, L., Stephan, C. "The Characterization of Nanoparticle Element Oxide Slurries Used in Chemical-Mechanical Planarization by Single Particle ICP-MS", PerkinElmer application note, 2014.

Table 2. Particle Size and Concentrations for three CMP Slurries.

	Particle Sizing		Particle Counting					
Sample	MPS (nm)	% RSD	Total Particles Counted	Particles > 100 nm	% of Particles > 100 nm	Particles >150 nm	% of Particles >150 nm
1	52.6	2	3279	387	11.8	49	1.5
2	42.1	1	2136	148	6.9	14	0.7
3	42.2	1	2005	148	7.4	14	0.7

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