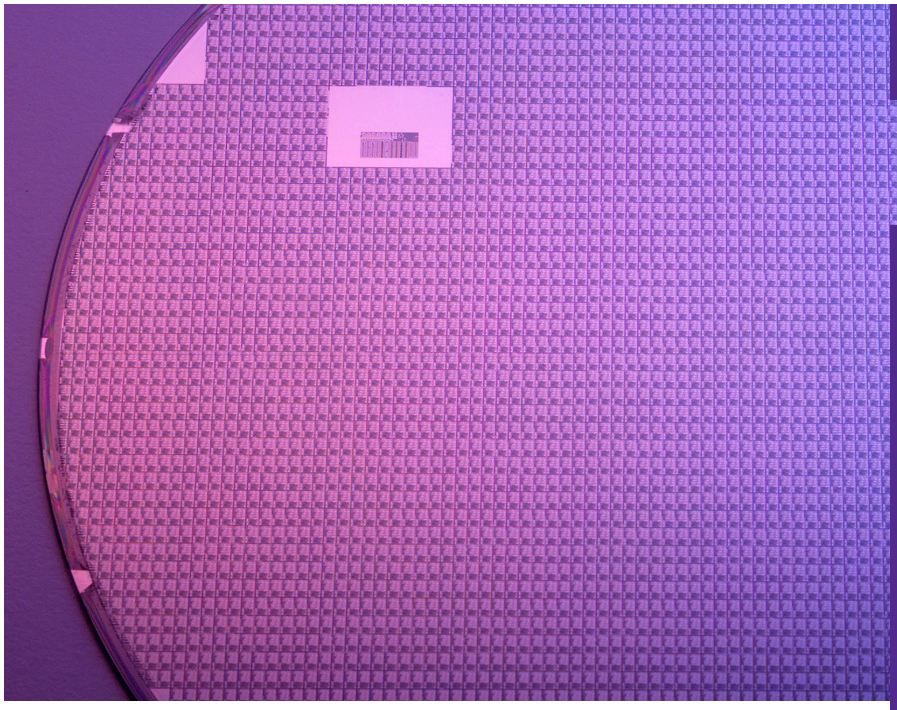

APPLICATION NOTE

ICP - Mass Spectrometry

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The Characterization of Nanoparticle Element Oxide Slurries Used in Chemical-Mechanical Planarization by Single Particle ICP-MS

Introduction

This study outlines the quantitation and characterization of element oxide nanoparticles (Al_2O_3, and CeO_2) commonly used in the nanoelectronics and semiconductor fabrication industry for the chemical-mechanical planarization (CMP) of semiconductor surfaces. CMP is a process of smoothing surfaces with the combination of chemical and mechanical forces in preparation for photolithography. The process uses various element oxide slurries and pressure to chemically and mechanically polish the silicon wafers during the manufacturing of semiconductor devices. In an effort to reduce size of the electronic device and improve the yield of the manufacturing process, CMP slurries consisting of nanoparticles are now in use.

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The characterization of the size distribution of CMP slurry nanoparticles, as well as the identification of larger particles, is an important aspect for the quality control of the photolithography process as they can impact the eminence of the silicon wafers. One of the most promising techniques for analyzing metallic nanoparticles is ICP-MS run in single particle mode (SP-ICP-MS). Due to its ability to measure both the dissolved concentrations of analytes and individual nanoparticles, an ICP-MS which is capable of measuring single particles is an ideal instrument for both types of analyses in the semiconductor industry.

Because of its sensitivity, flexibility, and analysis speed, SP-ICP-MS is gaining popularity for detecting and measuring inorganic-based nanoparticles. With this technique, nanoparticles are introduced into an ICP and completely ionized, with the resulting ions being detected by a mass spectrometer. The intensity of the signal is related to the particle size; thus SP-ICP-MS provides the user with particle concentration (particles/mL), size and size distribution.

In order to ensure that only a single particle is measured at a time, the sample has to be diluted to achieve temporal resolution between particles. The mass spectrometer must be capable of making extremely rapid measurements to ensure nanoparticle detection as the transient signal of a 50 nm nanoparticle can vary on average between 300 and 500 µs, depending on the instrument's operating conditions and ion optics design (Figures 1 and 2).

The kind of speed required for SP-ICP-MS is called "transient data acquisition speed", which is the number of data points the instrument can acquire for a single mass per second. The greater the transient data acquisition speed the instrument provides, the better it is for SP-ICP-MS. The PerkinElmer NexION® 350 ICP-MS operating in single particle mode is able to acquire data continuously, with the elimination of settling times, giving it the ability to acquire as much as 100,000 data points/second.

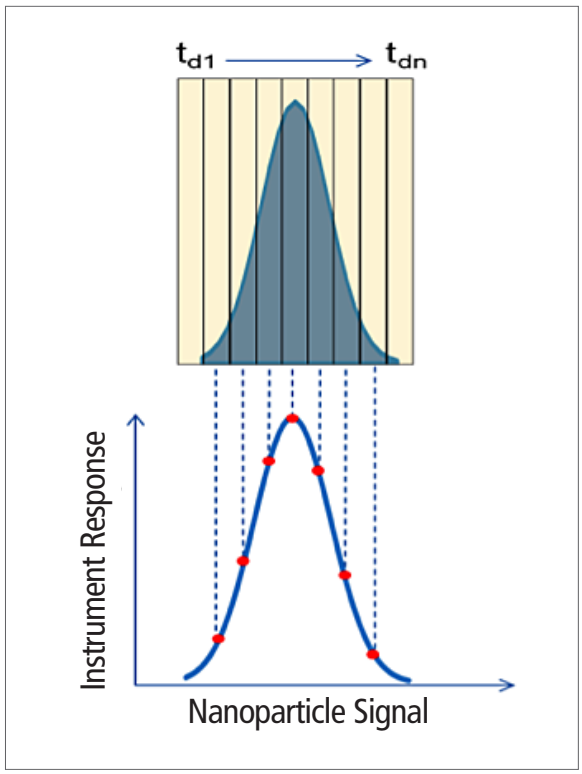

Figure 1. Acquiring data faster than the transient signal allows surface area integration of nanoparticle signal.

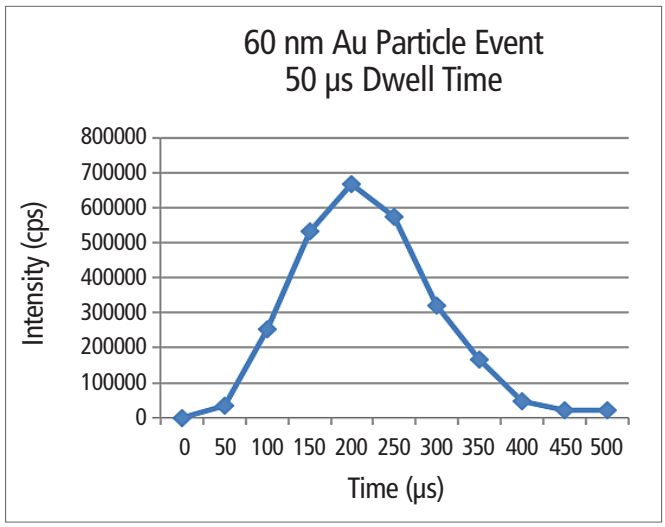

Figure 2. Signal of one gold 60 nm particle acquired using the NexION 350 ICP-MS operating in single particle mode (50 µs dwell time and no settling).

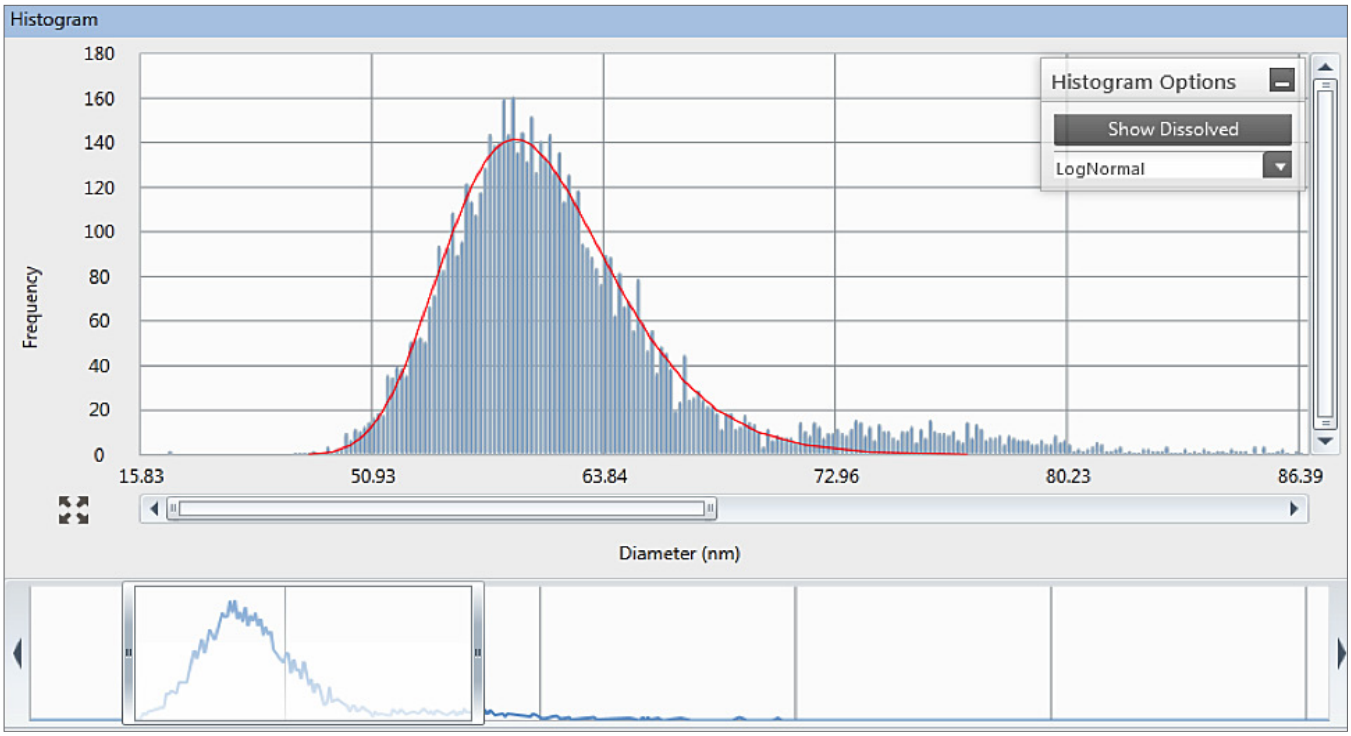

Figure 3. NIST SRM 8013 Gold 60 nm SP-ICP-MS size distribution graph.

Experimental

Sample Preparation

In preparation for SP-ICP-MS analysis, the sample slurries were ultrasonicated for 5 minutes and simply diluted in laboratory pure Type I water prior to analysis. Dilutions were calculated so that the final analysis sample liquid contained approximately 200,000 particles/mL. For most CMP slurries, this amounted to a dilution of between 10^6 and 10^7.

Instrumental

The instrument used in this work was a NexION 350D ICP-MS (PerkinElmer Inc., Shelton, CT, USA) – instrumental parameters and conditions are given in Table 1. Calibration curves for the elements were built from PerkinElmer Pure commercially available NIST traceable standards (PerkinElmer Inc., Shelton, CT). One blank and four calibration points were used. The system transport efficiency was calculated using two Ted Pella, Inc. (Redding, CA, USA) gold nanoparticle standards (50 and 80 nm) and validated using the NIST SRM 8013 (60 nm). Unlike conventional quadrupole ICP-MS systems, the NexION 350 in single particle mode completely eliminates the quadrupole settling time. The elimination of quadrupole electronics settling time provides for a truly continuous stream of data from the ICP-MS detector. By capturing data continuously and rapidly, the NexION ICP-MS does not miss any of the single particle events, resulting in precise particle counting and a greater number of events per period of time spent analyzing each sample.

Table 1. Instrumental Parameters and Conditions for SP-ICP-MS.

Parameter	Value
Instrument	NexION 350D ICP-MS
Nebulizer	PFA Concentric
Spray Chamber	Cyclonic
Torch and Injector	Quartz Torch and Alumina 2.0 mm ID injector
Power (W)	1600
Plasma Gas (L/min)	15
Aux Gas (L/min)	1.2
Neb Gas (L/min)	1.02
Sample Uptake Rate (mL/min)	0.25
Sample Tubing	Orange/Green
Dwell Time (µs)	100
Sampling Time (s)	60

Method Validation

Instrument validation was performed using the NIST SRM 8013 Gold Nanoparticles Nominal 60 nm Diameter as a quality control (QC). The size distribution of the NIST SRM 8013 Gold Nanoparticles is displayed in Figure 3. The graph shows good nano scale agreement with the certified value 60 nm. The Ted Pella gold nanoparticles are used to calibrate the instrument as well as establish the transport efficiency of the nebulized nanoparticle suspensions into the plasma; the NIST 8013 is used as a QC check on the calibration.

Results – CeO_2

Both slurry samples contain a wide distribution of CeO_2 nanoparticles. The normalized frequency graph for Slurry #1 (Figure 4) shows sizes that fluctuate from 12 nm to 42 nm with a mean size distribution of 22.3 nm. The cumulative graph shows that 80% of the measured nanoparticles are 30 nm or less with a prevalent amount of 12 nm particles (at 20%) and the majority of the nanoparticles in the 20-30 nm range. The normalized frequency graph for Slurry #2 CeO_2 (Figure 5) shows sizes that fluctuate from 22 nm to 76 nm with a mean size distribution of 47.8 nm. 80% of the measured nanoparticles are below 62 nm. There was also an elevated background signal which indicated that some of the Ce was dissolved into solution. The results for both slurry samples are summarized in Table 2.

Results – Al_2O_3

Like the CeO_2 samples, both Al_2O_3 slurries contain a distribution of nanoparticles. The normalized frequency graph for Slurry #3 (Figure 6) shows sizes that range from 28 nm to 58 nm with a mean size distribution of 44.4 nm. The cumulative graph shows that about 80% of the particles are less than 54 nm with 50% below 48 nm. There appear to be two dominant sizes: the first at 28-38 nm (27%) and the second around 50 nm.

The normalized frequency graph for Slurry #4 (Figure 6) shows that this slurry sample has an even distribution of sizes from 22 nm to 46 nm with a mean size of 32.5 nm. The cumulative graph shows that 80% of the particles are 38 nm and less. The results for both Al_2O_3 slurries are summarized in Table 3.

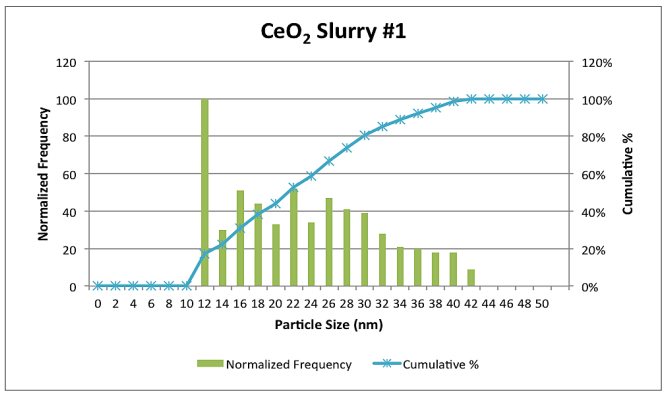

Figure 4. Slurry #1 normalized frequency particle size distribution graph.

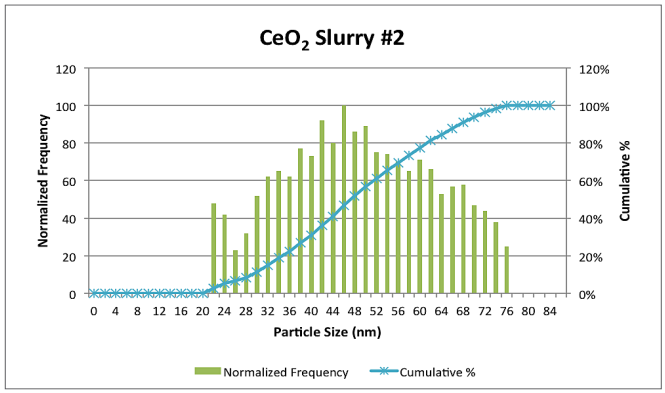

Figure 5. Slurry #2 normalized frequency particle size distribution graph.

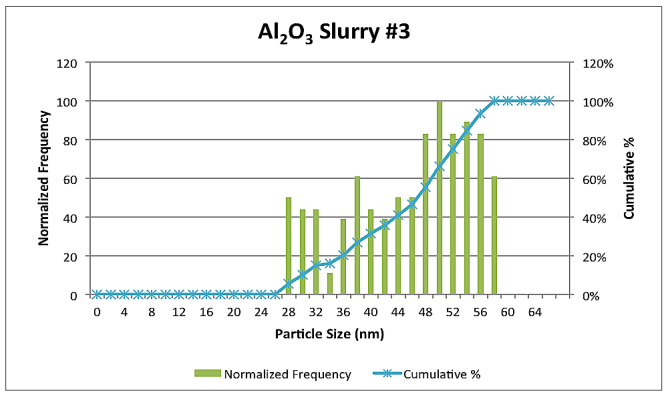

Figure 6. Slurry #3 normalized frequency particle size distribution graph.

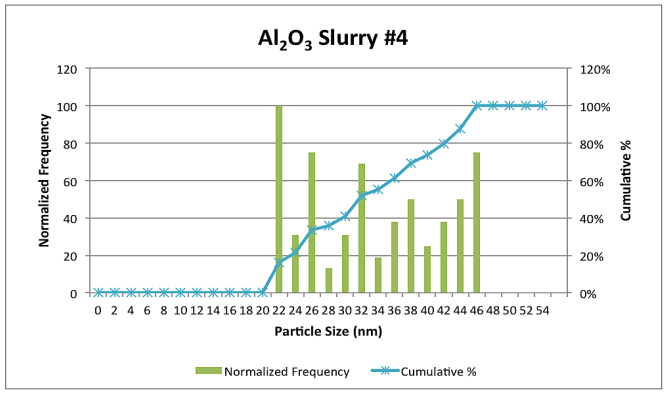

Figure 7. Slurry #4 normalized frequency particle size distribution graph.

Table 2. Results for CeO_2 Slurry Samples

Sample ID	Mean Size (nm)	Median Size (nm)	Particle Conc. (particles/mL)	Dissolved Conc. (ppb)
CeO_2 Slurry #1	22.3	21.4	196821	<0.01
CeO_2 Slurry #2	47.8	47.3	267029	0.13

Table 3. Results for Al_2O_3 Slurry Samples

Sample ID	Mean Size (nm)	Median Size (nm)	Particle Conc. (particles/mL)	Dissolved Conc. (ppb)
Al_2O_3 Slurry #3	44.4	47.2	122536	<0.02
Al_2O_3 Slurry #4	32.5	31.8	148960	<0.02

Conclusions

This work has shown how the NexION 350D ICP-MS in single particle mode was used to successfully characterize two types of element oxide nanoparticles. Results were given for mean and median particle size, particle concentration, as well as graphs of the size distribution and cumulative percentage of particles versus size. The acquisition of this data was achieved in a single, rapid analysis of the slurry samples tested.

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