Measuring Large Particle Contaminants in Cerium Oxide Chemical Mechanical Polishing (CMP) Slurries with Total Holographic Characterization

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ABSTRACT

Ceria-based slurries are widely used for polishing in semiconductor CMP processes. Previous studies have demonstrated that Total Holographic Characterization® (THC) is an effective technique to monitor agglomeration in silica slurries [1,2]. The work presented here extends this technique to the study of ceria slurries. Ceria nanoparticles have a higher refractive index than silica nanoparticles and therefore are more effective at scattering light. As a result, the background speckle caused by the native ceria nanoparticles is more significant, reducing the signal-to-noise ratio in measurements of large particle contaminants in ceria slurries, and making measurements more challenging. Large particle contaminants (LPC) in commercial CMP ceria slurries were successfully detected and characterized using THC. Robust, reproducible measurements are critical for monitoring the quality of CMP slurries. We demonstrate the robustness of THC in measuring LPC in CMP slurries samples, and compare different sampling approaches to optimize measurement reproducibility. Finding accurate, reproducible methods of measuring LPC in ceria slurries has been challenging because significant variability can be caused by sedimentation, sample handling, and sample inhomogeneity. Using a robotic sample handling system, we demonstrate reliable measurements of the concentration of large particle contaminants with THC.

INTRODUCTION

As the semiconductors move toward higher density integrated circuits with smaller feature dimensions and increased layers, effective polishing becomes more critical during wafer processing, and the quality of the CMP slurries becomes an even more important parameter in processing. A small percentage of large agglomerates in the CMP slurries can degrade surface quality and produce defects. Therefore, significant efforts have been introduced to monitor and characterize slurries at different stages of the CMP process.

In our previous work, we introduced Total Holographic Characterization (THC) to investigate contaminants in silica CMP slurries [1]. We demonstrated the effectiveness of THC in monitoring silica CMP slurries to measure the size and refractive index of the agglomerates and other contaminants without the need for dilution of the slurry [2]. In this work, THC is used to measure cerium oxide (CeO_2) or Ceria CMP slurries (NanoArc CE-6450 and Ultrasol Optiq). These slurries have been the abrasive of choice for CMP polishing for the optical [3] and semiconductor industries [4, 5]. Ceria slurries have better selectivity and removal rate for certain types of surfaces relative to silica slurries [3]. However, evaluating quality of ceria slurries presents a particular challenge for conventional optical methods [3]. The optical density of ceria CMP slurries at standard (0.1 to 5 wt%) concentrations [5, 6, 7] used in semiconductor CMP processes are typically too optically dense for most optical technologies, without significant dilution [8]. For most measurement techniques, ceria slurries must be diluted before measurements are possible. Dilution, however, changes the environmental conditions and therefore, may affect the concentration of agglomerates of the native nanoparticles of the slurry [1]. In addition, the denser ceria particles stain and easily stick to surfaces, often requiring significant cleaning and maintenance after each measurement [9]. Therefore, sample handling in characterizing large particle contaminates of these ceria nanoparticle slurries is another focus of the work here.

With THC, we successfully demonstrate the measurement of two different types of Ceria slurries. We also show how sedimentation and sample handling affect the concentration of agglomerates measured in ceria CMP slurries. With the help of a robotic sample handling system, we demonstrate that THC is a robust analytical technique that can characterizing large particle contaminants in Ceria CMP slurries.

EXPERIMENT

Total Holographic Characterization® is a patented technology that can reliably measure individual colloidal particle's size and refractive index simultaneously. The THC setup (xSight, Spheryx Inc.) used in this work has previously been described [1, 2]. In brief, THC uses a collimated laser as an illumination source. 30μL of sample was pipetted into a microfluidic device, (xCell8, Spheryx Inc.) as shown in Fig. 1. The use of single use disposal microfluidic devices also reduces cross contamination between measurements and reduces system down time for instrument maintenance.

Sample flows through the microfluidic device through the viewing area of dimension 150 x 100 x 55 mm^3. Particles larger than the wavelength of the illumination laser (λ(vacuum) = 445nm) scatter the laser and project an interference pattern, also known as a hologram, on the focal plane of a microscope objective as shown in Fig 1(b). The microscope objective magnifies and relays the holograms onto a video camera for recording as shown in Fig. 1(a). A multi-parameter fit was used to compare the recorded hologram with the standard model for light scattering (Lorenz-Mie theory) to extract the size and refractive index of the colloidal particles. Spheryx's implementation of THC is fast enough, to build up population distribution data within a short period of time, for tracking and monitoring concentrations of different dispersed populations of particles.

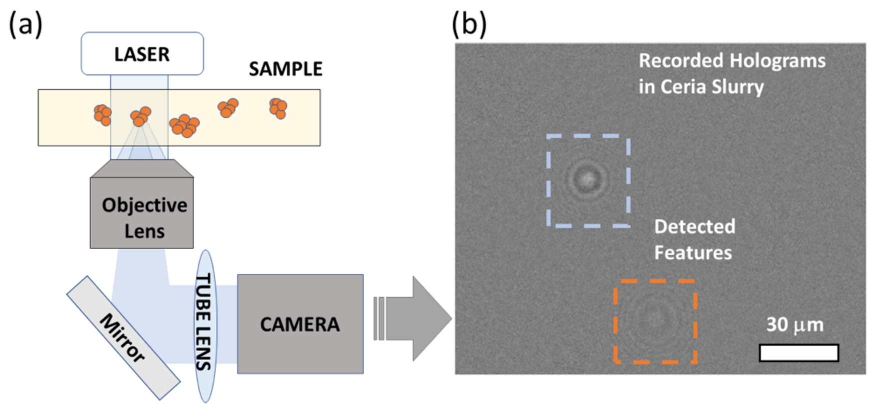

Fig. 1(a) A schematic describing how THC works. (b) An actual experimental image of holograms detected in ceria CMP slurry.

In this work, we also introduced a robotic sample handling system, (xStream, Spheryx Inc) for automatic mixing and slurry sample delivery to the holographic characterization instrument (xSight, Spheryx, Inc.) for consistent results. The xStream is able to deliver 96 different samples for unsupervised measurement with the xSight system. xStream is also designed with an automatic sample mixing algorithm to mitigate the effect of sedimentation within samples.

RESULTS AND DISCUSSION

THC can measure particle in the size range from 500nm to 10 μm. In the measured data, native nanoparticles used in slurries are normally not visible as individual particles, and only contribute as speckle background noise [1]. In some cases, however, because cerium oxide had a very high index of refraction, nanoparticles can be detected and characterized at smaller sizes, sometimes as small as a couple hundred nanometers, as shown in Fig 2(a). Fig. 2(a) shows the analysis of both the native particles and larger agglomerates of Ultrasol Optiq ceria slurry. The native 400nm ceria particles were determined to have an index near 2.0. The larger agglomerates were determined to have a refractive index closer to the medium index at 1.34. For ceria slurries with smaller native particles, such as NanoArc CE-6450 which has 30nm nanoparticles, the native particles are not visible to the instrument. As shown in Fig. 2(b), only the larger agglomerates were detected in this slurry.

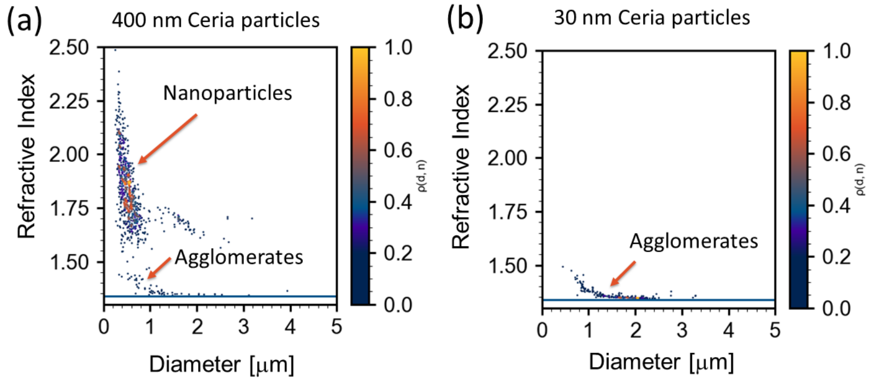

Fig.2 Scattered plot size against refractive index of ceria slurry samples (a) Ultrasol Optiq and (b) NanoArc CE-6450

Another advantage of holographic characterization is its ability to measure agglomerate concentration accurately and reproducibly. THC measures particle concentrations from $1x10^3$ to $1x10^7$ particles/mL for large particle contaminants. NanoArc CE-6450 (1 wt %) is a typical slurry composition for semiconductor processing. Different concentrations of polystyrene beads were added to this ceria slurry to evaluate concentration measurement accuracy. The results are shown in Fig 3. Known concentrations of standard 0.7μm polystyrene beads (PS03N, Bangs Laboratories, Inc.) were added to the ceria slurry before (Fig. 3a) and after filtration of the slurry (Fig. 3b). The measurement of the concentration of the beads were consistent with the prepared concentration of the beads, both before and after filtration, over the range of concentration of 10^5-10^6 particles/mL.

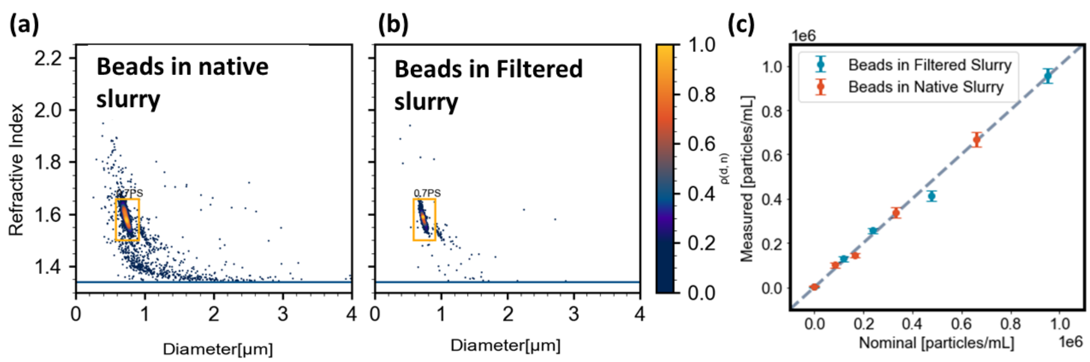

Fig.3 (a) Scatter plot of NanoArc CE-6450 doped with polystyrene beads (diameter = 700 nm). (b) Scatter plot of NanoArc CE-6450 after filtering and doped with the same beads. (c) Dilution studies of different concentrations of microbeads in the two preparations of ceria slurries.

Fig 3(c) showed the linear relationship of the measured concentrations of beads with the different nominal concentrations of polystyrene beads added to the ceria slurries.

In many cases, the density of particles in the slurry causes them to gradually sediment over time, creating inhomogeneity in concentration over the volume of the slurry. Fig 4(a) shows two samples that were prepared. One sample consisted of 1.5 μm polystyrene beads (NT16N, Bangs Laboratories, Inc.) in deionized water. The second sample consisted of ceria CMP slurry (CE6450) at 0.2 wt % solid concentration. For these sedimentation experiments, the samples were left undisturbed for more than a day before measurements. After the resting period, each sample aliquot was extracted from the samples from four segments (Top, Upper, Lower and Bottom) of the vial, as shown in Fig. 4(a).

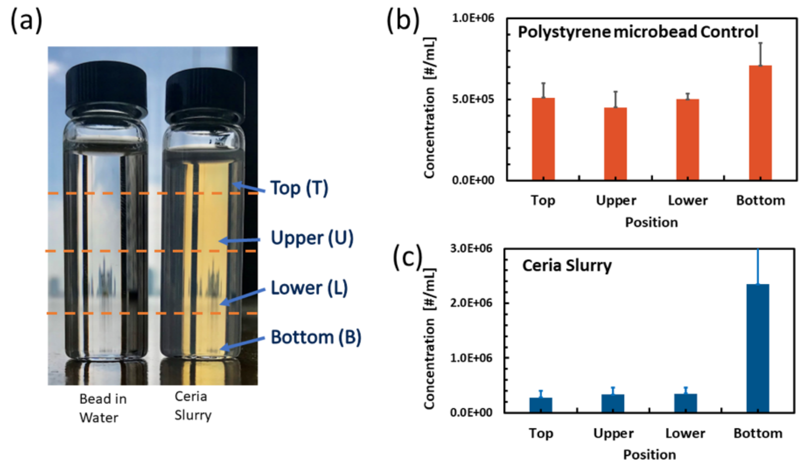

Fig.4 (a) Photographic images of 1.5μm polystyrene microbeads in water and 30nm ceria slurry. (b) Measured concentration of polystyrene microbeads at different positions of the sample bottle. (c) Measured concentration of agglomerates at different positions of the sample bottle.

Fig. 4(b) shows the results of the measurement of the concentrations of polystyrene beads as a function of position in the vial. Small fluctuations in the concentration of polystyrene particles measured at the different positions are observed. Fig 4(c), shows the results of the same experiment conducted on the ceia sample. The variability of the concentration of particles detected in the ceria slurries showed significantly more variability. Agglomerate concentration measured at the bottom of the vial was significantly greater that those observed at the other three positions of the vial. The higher concentration of the agglomerate concentration at the bottom of the vial in the ceria sample suggests that sedimentation is causing significant inhomogeneity in the sample. These results demonstrate the importance of consistent sample handling when making comparative measurements of a slurry over time.

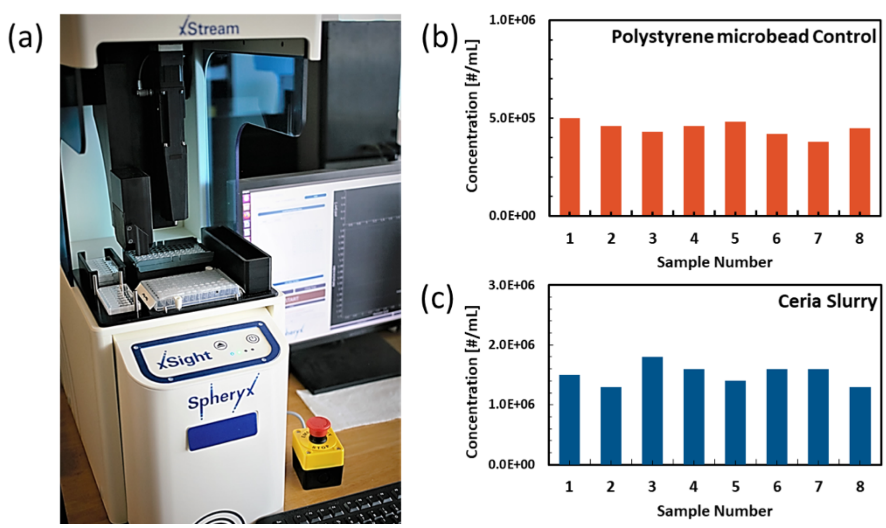

Fig.5 (a) Photographic image of the robotic sample handling setup with the THC instrument. (b) Plots of concentration of polystyrene beads in water for eight independent measurements. (c) Plots of concentration of particles detected in eight independent measurement of ceria slurries in Fig 4.

A robotic sample handling system, (xStream, Spheryx Inc.) was introduced for automated sample mixing and sample delivery of slurry to the holographic characterization instrument (xSight, Spheryx Inc.) to increase the uniformity of sample preparation, and therefore increase the reproducibility of concentration measurements in the slurry. Fig. 5(a) showed the integration of the robotic sample handling system, xStream, with xSight for use in these experiments. xStream automatically loads the microfluidic device (xCell8) onto the xSight. Then, it performed pipette mixing of the sample three times before pipetting 30 μL into the sample well of the xCell8 for measurement. The same two samples of polystyrene beads and ceria slurries, as shown in Fig. 4, were used in these experiments. Results using automatic mixing and sample delivery showed consistency across all eight measurements of polystyrene microbeads samples (Fig. 5(b) and ceria slurries (Fig. 5(c)).

In addition to consistent concentration measurement, the measured size distributions (Fig 6(a)) and refractive index distributions (Fig. 6(b)) of the ceria slurry samples also showed reproducibility across the eight experimental replicates. The size distribution had a median size of 1.22 ± 0.02 μm and refractive indexes of 1.376 ± 0.001.

When different sample handlings (sedimentation, manual mixing, and robotic handling) of the same samples were compared, the robotic handling provided the most consistent results for particle concentrations of both polystyrene beads and slurry agglomerates as shown in Fig 6(c). The largest variations resulted from measurements where the samples were allowed to sediment for more than 24 hours. The measured concentrations were highly dependent on the position where the sample was extracted from the container.

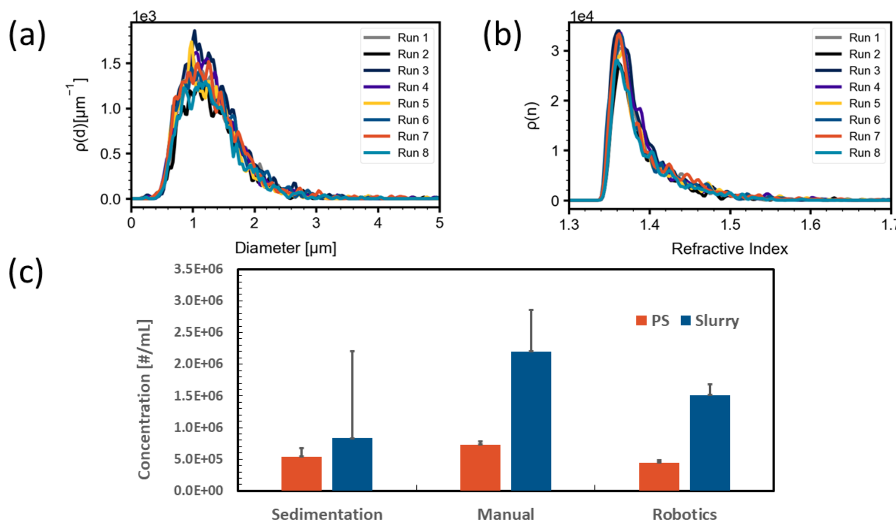

Fig.6 (a) and (b) are size and refractive index distributions of ceria slurry respectively. Eight independent measurements of the samples showed the robustness of using holographic particle characterization to measure ceria slurries samples. (c) Plots showing three different methods of sample handling of the sample in Fig. 4.

CONCLUSION

In this work, we successfully demonstrated using holographic characterization to detect and characterize commercially available ceria CMP slurries. We showed the accuracy in using this approach in determining the concentration of contaminants in the slurries. In addition, THC was also shown to give accurate and consistent measurement of agglomerate concentration in ceria CMP slurries. Using a robotic sample handling system with THC, we demonstrated that THC reliably measured agglomerate concentration reproducibly in ceria CMP slurries.

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