Holographic Characterization of $KMnO_4$ based CMP slurries for SiC polishing

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ABSTRACT

This work presents the analysis of high precision polishing slurries with potassium permanganate ($KMnO_4$) additives using Total Holographic Characterization® (THC). These slurries are formulated for the chemical mechanical planarization (CMP) of silicon carbide wafers. The purple potassium permanganate stains surfaces and has a large absorption coefficient for visible light. The combination of potassium permanganate and the abrasive nanoparticles that make up the CMP slurries presents a challenge for quality monitoring during the slurry blend and delivery process using most optical techniques. THC has proven effective in detecting agglomerates in turbid CMP slurries [1] containing a variety of different compositions of nanoparticles [2]. In this work, we extend THC to characterizing slurries containing permanganate additives. Samples of slurries containing permanganate were measured without any need for dilution or calibration. This approach was demonstrated to be robust and effective in detecting large particle contaminates in slurries with $KMnO_4$ additives.

INTRODUCTION

In high power and high temperature applications, silicon carbide (SiC) wafers are the material of choice [3, 4]. SiC is a physically hard and chemically inert material [5] which can withstand high temperature. These same characteristics also make polishing SiC wafer into a flat and deflect free surface with conventional CMP polishing challenging [5]. One solution is to add a strong oxidant, such as $KMnO_4$, to CMP slurries to achieve high removal rate with a high quality surface for SiC wafers [6,7].

The purple $KMnO_4$ slurries stain surfaces easy and have a large absorption coefficient for visible light. Fig. 1 shows an example of the staining caused by slurries with $KMnO_4$. Therefore, the combination of potassium permanganate and the native nanoparticles that make up the CMP slurries presents a challenge for quality monitoring using most optical techniques during the slurry blending and delivery process.

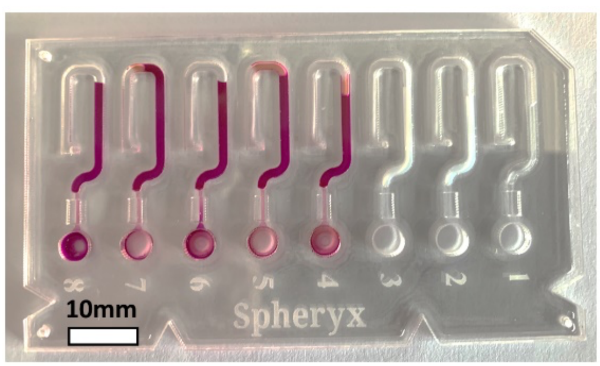

Fig.1 Photographic image of the disposable microfluidic chip xCell8 after use. The first 3 channels were used to measure slurries without $KMnO_4$ and the next 5 channels were used for measurements of slurries with added $KMnO_4$. Scale bar represents 10 mm

In this work, we introduced Total Holographic Characterization® (THC) as a tool for particle characterization to determine agglomerate concentrations and size distributions, as well as the characterizing native CMP particles in slurries with $KMnO_4$.

EXPERIMENTAL SETUP

Total Holographic Characterization® (THC) uses holograms of individual particles to determine the particle's size and refractive index simultaneously. In earlier work, we demonstrated the ability to use this approach for quantitative analysis of particles in turbid media [1] and in characterizing agglomerates in different types of CMP slurries [2].

Our measurement system (xSight, Spheryx, Inc.) illuminates the sample with a collimated laser beam operating at a vacuum wavelength of $\lambda = 445$ nm. Thirty microliters of sample is pipetted to the microfluidic device (xCell8, Spheryx, Inc.) for each run. Each xCell8 can be used for up to eight independent measurements. A precise volume of sample is pulled through the microfluidic channel on xCell8. The flow of the sample is automatically controlled by the instrument. If a particle passes through the detection region, it scatters the incident laser beam. The scattered light interferes with the remainder of the beam to form an interference pattern known as a hologram. The objective lens magnifies and relays the hologram to a CCD camera which records the hologram. The recorded hologram is analyzed using a multiparameter optimization of images predicted by Lorenz-Mie theory. The optimized parameters provide the best fit of the size and refractive index of the scattering particle.

The microfluidic sample cell provides multiple advantages for applications involving dyes such as $KMnO_4$. During the measurement, the sample remains in the xCell8, moving from the sample reservoir, through the measurement channel and into the waste reservoir as shown in Fig. 1. No sample enters the instrument and therefore prevents any cross contamination between samples, or permanent staining of reusable components within the instrument. In Fig. 1, slurries without any $KMnO_4$ are contained in channel 1 to 3 of the sample cell and slurries with purple $KMnO_4$ are contained in channels 4 to 8 of the sample cell. After eight runs, the disposable sample cell is replaced and measurements proceed without any need for cleaning between measurements.

Once the sample is analyzed, probability distributions in both size and refractive index describe the population of particles in the sample. Examples of scatter plots of particle refractive index versus particle size are shown in Fig. 2 and the probability distribution in size and refractive index of both samples are shown in Fig. 3. The refractive index distribution provides information about the composition of the particles, in addition to the size of the particles. The combination of both size and refractive distribution is a unique fingerprint of the particle population in the sample.

THC measures particles from 500 nm to 10 μm in size and from 1.3 to 1.7 in refractive index. THC can also accurately measure particle concentration from $1\text{x}10^4$ particles/mL to $1\text{x}10^7$ particles/mL.

Two types of CMP slurries: Slurry A (smaller native nanoparticles) and Slurry B (larger native nanoparticles) were analyzed with THC in this study. $KMnO_4$ was added to both types of slurries.

RESULTS AND DISCUSSION

Fig. 2 presents results of the analysis of the slurries. Fig. 2(a) shows results for a sample of the native abrasive nanoparticles. The abrasive nanoparticle slurry has few large particle contaminants. Slurry A native particles are much smaller than 500nm, and below the threshold for detection. For most CMP slurries, the nanoscale native particles are not detected, and only increase the background speckle [1]. When particles aggregate to form agglomerates that are larger than 500nm, THC detects and characterizes them. Since the native particles are not detected, larger particles are easily detected, usually without the need for dilution of the slurry. [1,2].

When $KMnO_4$ was added to slurry A, the scatter plot changed significantly, as shown in Fig 2(b). There are two different populations present in Fig. 2(b). Both populations consist of particles larger than 1 μm. One population has a refractive index >1.5 (yellow box) and the other population has a refractive index lower <1.4 (blue box).

In a separate slurry sample, slurry B, with $KMnO_4$, there were two unique populations as shown in Fig. 2(c). Both populations had refractive index >1.5. One population consisted of particles smaller than 1 μm (mean 450nm) and the second population were particles larger than 1 μm (mean 1.68 μm). The population of smaller particles are of a size and index consistent with the native particles of slurry B as provided by the manufacturer of the slurry. The high index of these particles is consistent with metal oxide particles.

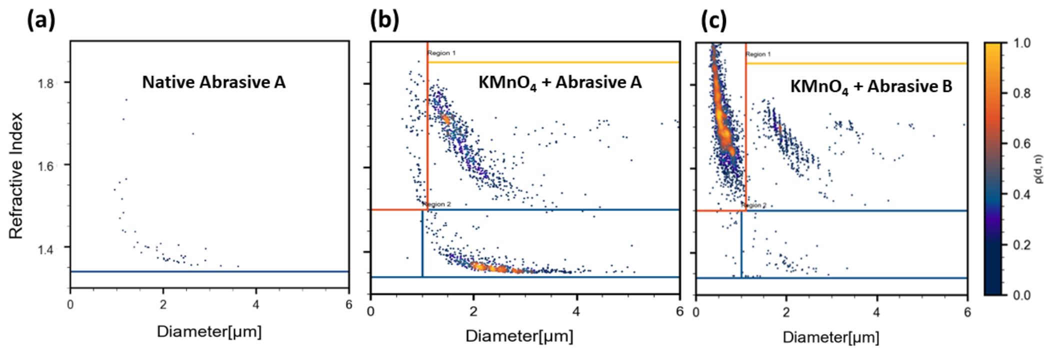

Fig.2 (a) and (b) are scatter plots of refractive index verses particle diameter of slurry A without $KMnO_4$ and with $KMnO_4$, respectively. (c) Scatter plot of refractive index verses particle size of slurry B with $KMnO_4$ added. The color of the points represents the probability density for a give size and index.

In this work, each sample was measured three times. The reproducibility of the measurements of the same sample is shown in Fig. 3. Fig. 3(a) and 3(b) show the probability distributions of particle diameter and index respectively for 3 measurements of sample A. Fig. 3(c) and 3(d) show the same probability distributions for sample B. These experiments show the sensitivity, reproducibility and robustness of holographic characterization in the detection of agglomerates in slurries with $KMnO_4$.

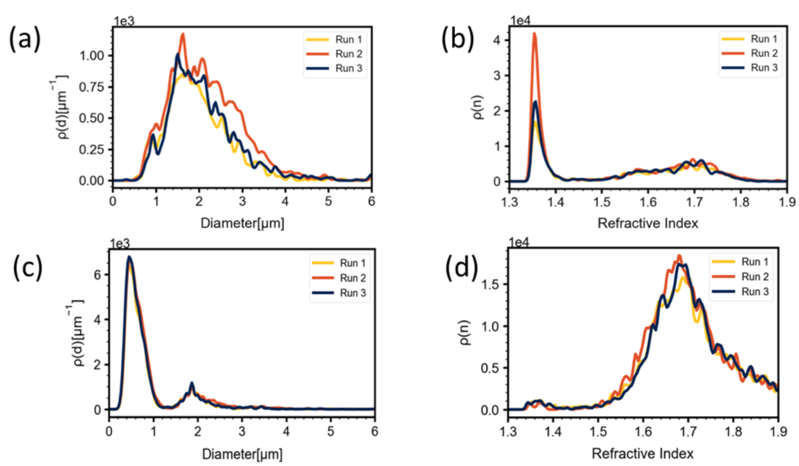

Fig.3 shows three independent measurements of both Slurry A and B with $KMnO_4$. (a) and (b) are the probability distribution of the diameter and refractive index of the particles in sample A respectively. (c) and (d) are the corresponding size and refractive index distributions for sample B.

CONCLUSION

The results in this work demonstrate that CMP slurries with $KMnO_4$ can be effectively characterized using Total Holographic Characterization. All measurements were made without the need for dilution. Species with a strong absorption coefficient, such as $KMnO_4$, do not interfere with THC analysis. In addition, the disposable microfluidic chip, xCell8, eliminates cross-contamination and the need for cleaning. Holographic characterization can be an effective and reliable tool to measure large particle contaminants in slurries with $KMnO_4$ additives.

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