

# Particle size distribution shift as a predictor of slurry stability

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**Abstract** - As device dimensions shrink, increasing efforts are made to reduce micro- and sub micro-scratches. Liquid particle count (LPC) has traditionally been used to quantify slurry particles that may cause scratch defects during the chemical mechanical planarization (CMP) process, with a subsequent reduction in wafer yield. However, LPC has historically had a limitation in that the method could only detect relatively large particles, typically > 0.5  $\mu\text{m}$ . For future advanced (small) nodes, micron and sub micro-scratches may be generated by particles < 0.5  $\mu\text{m}$ . In this paper, it will be demonstrated that particle size distribution (PSD) can be used as a more accurate metrology than LPC in predicting scratches. Furthermore, it will be demonstrated that PSD can be stabilized by the ingredients in the formulation.

## Introduction

An increase in scratch formation during the CMP process is the greatest concern related to particle agglomeration. Typically, scratches are generated by by-products such as large particles and agglomerated particles in a slurry and pad debris with abrasion between the wafer and pad [1]. Large abrasive particles has historically been linked to an increase in scratches [2, 3]. Recently, a strong correlation was found between defects and the total particle count in the smallest (1.0-1.2  $\mu\text{m}$ ) LPC bin for Vantage SlurryScope system [4]. A previous study reported that not only coarse (hard) particles but also soft agglomerates of the primary abrasive particles must be avoided in the polishing slurries to ensure acceptable surface quality [5]. However the correlation between small size of particles and scratches remains unclear.

Accurate particle size measurement is a major technical challenge. Slurries composed of ceria nanoparticles in the range 100-400nm have been characterized by the analysis of the optical forwarded-scattered field [6]. In addition, fluorescence correlation spectroscopy (FCS) has been demonstrated to be an effective

characterization tool in the analysis of silica abrasives (< 20 nm) used in CMP slurries [7]. More mature technologies for measuring PSD is Light Scattering (LS) and Dynamic Light Scattering (DLS). LS techniques are based on the principle that light scatters more intensely and at smaller angles off of large particles than small particles [8, 9]. Several technologies, e.g. Horiba LA-9XX series (e.g. LA-950), utilize light scattering to determine PSD [10]. The tool measures the angle and intensity of light scattered from the particles in the sample. That information is then passed to an algorithm designed to use Mie Scattering Theory which transforms the scattered light into particle size information [11]. One possible limitation of "Mie scattering" is that the size of scattering particles is suggested to be comparable to the wavelength of the light, and may not accurately detect wavelengths that are much smaller or much larger than that of light. DLS is used for determining PSD by measuring the random changes in the intensity of light scattered from a suspension or solution [10, 12]. Small particles in suspension undergo random thermal motion known as Brownian motion, which is modeled by the Stokes-Einstein equation. For particle size analysis, the equation is typically given in this form:

$$D_h = \frac{k_B T}{3\pi\eta D_t}$$

where  $D_h$  is the hydrodynamic diameter (i.e. particle size),  $D_t$  is the translational diffusion coefficient,  $k_B$  is the Boltzmann's constant.  $T$  is the thermodynamic temperature and  $\eta$  is the dynamic viscosity.

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A new development in PSD measurements came with the introduction of the UPA system (e.g. UPA-151) by Microtrack in 1990 [13]. In this method, a so-called controlled reference method is used, which increases the optical signal to the photodetector system up to a million times compared with traditional DLS, providing the possibility for improved nanoparticle size analysis capability.

Our study demonstrated that PSD measured by DLS technique is capable of more accurate detections of particle size changes resulting from agglomeration in aging slurry. PSD also correlated better with the scratch counts on the wafer compared with LPC. In addition, it was demonstrated that PSD shift can be stabilized by optimizing some of physical properties and ingredients in the slurry.

## Results and discussion

### Experiment 1

LPC and PSD changes may occur over time in CMP slurries. To expedite the slurry aging process, two slurries (“A” and “B”) were aged through storage at an elevated temperature (5 days at 80° C), and LPC and PSD were investigated for fresh or aged slurries A and B. The particles and key features of the chemistry for two slurries used in this experiment are summarized in Table 1. Both slurries used particles with PSD Medians below 150 nm.

Slurry	Particle	Additive	pH
A	A	A	4.0
B	B	B	2.8

Table 1. Particles and key features of the chemistry for slurries A and B.

As seen in Table 2, slurry A exhibited a significant increase in LPCs after aging (87-times increase), while slurry B did not significantly exhibit an LPC increase after aging. Therefore LPC results indicate there is no significant increase in particles (> 0.56  $\mu\text{m}$ ) for slurry B. On the other hand, Table 3 showed that both slurries exhibited an increase in PSD Medians (10.6-times increase for aged slurry A and 1.5-times for aged slurry B), suggesting that PSD measurement with UPA-151

is capable to detect the changes in particle sizes below 0.56  $\mu\text{m}$ .

	Fresh	Aged
<b>Slurry A</b>	1.0	87.0
<b>Slurry B</b>	1.0	0.9

Table 2. Normalized LPC (> 0.56  $\mu\text{m}$ ) for fresh or aged slurries A and B. LPCs were measured by Accusizer 780 AP and normalized against fresh slurry.

	Fresh	Aged
<b>Slurry A</b>	1.0	10.6
<b>Slurry B</b>	1.0	1.5

Table 3. Normalized PSD Medians for fresh or aged slurries A and B. PSDs were measured by Microtrack UPA-151 and normalized against fresh slurry.

To determine the correlation between scratches and changes in LPC and PSD, scanning electron microscopy (SEM) was used to determine the scratch number on blanket Tetraethyl ortho silicate (TEOS) wafers. In Table 4, slurry A exhibited a significant increase in scratches after aging (180 and 1241 scratches for fresh and aged slurry A respectively), which correlated with an increase in both LPC and PSD, as shown in Tables 2 and 3. Interestingly, slurry B also exhibited an increase in scratches after aging (34 and 122 scratches for fresh and aged slurry B respectively), although no significant increase in LPC was obtained as shown in Table 2. The increase in scratches for slurry B can be attributed to an increase in PSD. A greater increase in scratches for aged slurry A might be attributed to a greater increase in PSD compared with slurry B, suggesting a correlation between the degree of PSD shift and the number of scratches.

	Fresh	Aged	% increase in scratches
<b>Slurry A</b>	180	1241	691
<b>Slurry B</b>	34	122	359

Table 4. Scratch counts on the TEOS wafer and percent increase in scratches for fresh or aged slurries A and B.

Our results indicate that a significant increase in PSD median (“shift”) can be obtained without an increase in LPCs, and that a PSD shift as small as 50% correlates with > 300% increase in scratches for aged slurry B. The PSD Median for fresh or aged slurry B was < 150 nm which is below the minimum detectable particle size for LPC. Sub-micron scratches, shown in Figure 1, might result from an increase in the size of the smallest particles in a slurry. In that case, sub-micron scratches could be predicted by a PSD shift on the order of  $\leq 50\%$ .

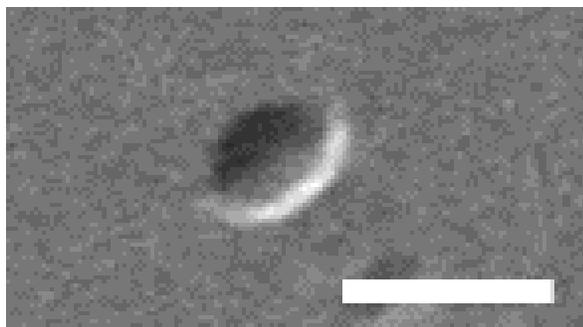


Figure 1. SEM picture of a sub-micron scratch on TEOS wafer. Scale bar indicates 200 nm.

## Experiment 2

To investigate the effect of different ingredients (particles and chemicals) in the slurry on PSD Median, four slurries (“B”, “C”, “D”, and “E”) were examined in this experiment. The key features of the samples are summarized in Table 5. All slurries used particles with PSD Medians below 150 nm. To discuss smaller change in PSD, the slurry was aged through storage at a lower temperature than in experiment 1 (10 days at 55° C). As shown in Table 6, a substantial variation in PSD Medians for aged slurries was observed for the different samples. Slurry C showed no change

in PSD Median after aging, suggesting PSD Median was significantly improved by particle change from type B to A. Both additive and pH changes resulted in bigger changes in PSD Median compared with slurry B. This study suggests the parameters such as particle, additive and pH significantly contribute to PSD stability. PSD shift issue for slurry B was resolved with an optimized particle. The scratches for slurry C will be studied further to support our model.

Slurry	Particle	Additive	pH
B	B	B	2.7
C	A	B	2.7
D	B	A	2.7
E	B	B	4

Table 5. Particle type, additive type and pH for slurries “B”-“E”.

Slurry	Parameter	Fresh	Aged
B	-	1.0	1.2
C	Particle	1.0	1.0
D	Additive	1.0	1.3
E	pH	1.0	2.8

Table 6. Normalized PSD Medians for fresh or aged slurries B-E. PSDs were measured by Horiba LA-950 and normalized against fresh slurry.

## Conclusions

In this study, it is demonstrated that a positive shift in PSD can be used to predict an increase in scratches, including cases when changes in LPCs are not detectable. It is also demonstrated that both type of particle and chemical mix parameters (additive and pH) can have an influence on particle stability and that PSD can be stabilized with an optimized particle. These results suggest that the introduction of PSD as a key metric in slurry development for the most advanced technology nodes could contribute to significant improvements in wafer yield.

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