Techniques to Measure Size of CMP Slurries

SPOS vs Laser Diffraction

PARTICLE SIZE ANALYSIS OF CMP SLURRIES: SPOS VERSUS LASER DIFFRACTION

The semiconductor industry is moving toward smaller line widths and more layers. One of the most important process considerations that will lead the way to this higher density chip technology is more sophisticated control of the planarization steps. The planerization, or polishing steps, are effected by the use of colloidally dispersed metal oxide slurries primarily silica and alumina (chemical-mechanical planerization or CMPs), with mean diameters in the 10 – 200 nm range. These slurries are applied to spinning polishing pads where the wafers rest. In the past, laser diffraction was most commonly used to characterize the particle size distribution of these slurries. It has always been known that these slurries contain a small volume percentage of particles greater than 1 micron in size. It is believed that these particles can cause scratches and other defects in the wafer surfaces. This paper will demonstrate that by virtue of the nature of the measurement, laser diffraction is inadequate to the task of quantitatively determining the concentration of out of specification slurry particles. On the other hand, single particle optical sizing (SPOS) because it counts particles, will be shown to be an excellent tool for characterizing CMP slurries.

One of the most important process control parameters involved in the manufacturing of high density integrated circuits is the performance quality of the polishing or planarization slurries. These slurries are used to produce a two dimensional surface after a lithographic or deposition step. It is very important that the CMP slurry not induce defects into the wafer during polishing. It has long been known that defects are caused by the presence of large "out of spec" particles. Some of these outliers are aggregates of the primary slurry particles while others are contaminates introduced during use. Considering the aggregation aspect first, one must realize that colloidal systems are thermodynamically unstable. Also, changes in the chemistry brought about by improper mixing, or the application of pumping action (shear), can accelerate the eventual break down of the slurry. Further complicating the issue is the second aspect, the considerable

handling CMP slurries undergo prior and during use. For example, certain slurries come in several parts (part chemical and abrasive) and require mixing. Silica slurries usually are sold in concentrated form and are diluted onsite. It is possible for contaminates to be introduced in the slurry during these preparation procedures. Furthermore, slurries are usually stored in large containers, called totes, from which the polishing machines draw material. In some arrangements, the totes are stored several floors below the fab requiring pumps to transport slurry over large distances (30 – 50 feet). It is possible that the shear can cause the slurry to aggregate. The slurry may separate or segregate over the distance from the tote to the polisher, changing the performance characteristics of the material. In any case, in the course of slurry preparation from storage area to use, there is ample opportunity for the introduction of contaminates that can cause defects as well, as various environments which may cause the slurry to become unstable and aggregate with time. So any improvement in the planerization process would require the quantification of the slurry polishing performance. The most obvious approach should be the detection of the presence of large defect causing particles. It would seem sensible to make use of the large array of particle sizing technologies for this task. A commonly used technique is laser diffraction (LD). LD was made popular because these instruments have large dynamic ranges and fast measurement times. But LD devices have serious limitations that are inherent in the physics they are based on. Laser Diffraction by definition is an ensemble technique. It requires a relatively complex and fundamentally "ill conditioned" mathematical algorithm to obtain an approximate representation of the particle size distribution (PSD). The "signal" which is obtained from a sample of the appropriate concentration is a "pattern" of scattered/diffracted intensity vs. angle. This pattern results from many particles being illuminated by the laser light source at the same time, where all of their individual scattered/diffracted light rays mix together at each detector element. The resulting pattern of scattered/diffracted light rays mix together at each detector element. The resulting pattern of scattered/diffracted light intensity

vs. angle no longer resembles a simple alternation of maxima and minima. The entire set of detected intensity values (suitably averaged in time) must be "inverted" and "massaged" by an appropriate mathematical algorithm in order to obtain, a reasonably accurate and reproducible estimate of the underlying PSD.

While LD is thought of as a single method, in fact, it is based on a combination of two physical principles: Fraunhofer diffraction and Mie scattering. The former relies on the pattern of scattered light intensity caused explicitly by the phenomenon of diffraction. The diffracted light intensity is detected over a range of relatively small angles with respect to the forward laser beam direction using a suitable spatial array of detector elements. In theory, the angular extent of the pattern of alternating maxima and minima in diffracted light intensity varies inversely with the diameter of the spherical particle, all other physical parameters (e.g; wavelength) being fixed. The larger the particle, the smaller the pattern.

However, the spatial pattern of periodic intensity variations due to the phenomenon of diffraction no longer exists for particle diameters smaller than approximately 2 mm. Instead, the mechanism, which is operative, is that of light scattering. Hence, in order to obtain even moderately reliable size information for particles smaller than this lower Fraunhofer "limit," which comprises almost the entire population distribution of typical CMPs, a second measurement based on Mie scattering theory, must be implemented. This theory describes the variation of scattering intensity at relatively large angles due to the mutual interference of individual light waves scattered from different points within a single particle. This effect gives rise to an angular dependence in the scattering intensity, which depends on the laser wavelength, the particle diameter, and the index of refraction of the particle.

In addition, the variation of scattering intensity with angle is also influenced significantly by the extent to which the particles absorb light. This factor is accounted for by the imaginary part of the (complex) index of refraction of the particles. Hence, the user must be prepared to provide both the real and imaginary components of the index of refraction of the slurry particles. Finally, in order to be effective, a "light scattering" instrument must successfully combine the results of its Fraunhofer diffraction and Mie scattering analyses, in order to produce accurate and reliable results for PSDs which overlap both physical regions

and theories. Constructing the correct "admixture" of results from two altogether different physical phenomena constitutes a difficult, and largely unsolved, technical challenge for instruments which are based on these two physical principles.

Of course, LD can be relatively effective in yielding a reliable mean particle diameter for CMPs, provided the underlying PSD for the sample is relatively simple and "well behaved." For stable, good polishing slurries, this criterion is often met; although we'll see an example below in which this assumption fails badly. However, in the case of unstable or bad slurries, for which the population of large outlier particles has grown significantly, the PSD is often no longer amenable to accurate, reliable analysis by a light scattering method. Instead, unacceptably large, and usually not reproducible, artifacts frequently result in the computed PSD.

In contrast, SPOS is a single particle counter based on light obscuration. By virtue of counting particles, SPOS can provide unparalleled resolution and sensitivity in the size range where most defect causing particles are found (see Application note 156). Because the PSDs in SPOS are built up one particle at a time, it is fund-amentally immune to the kinds of instabilities and artifacts the reported PSDs obtained from LD exhibit. SPOS permits one to obtain accurate and reproducible quantitative information concerning the region of the largest slurry particles. This is the very region that is of greatest importance to slurry performance. Let us contrast these two techniques by looking at some representative data. Figure 1a contains the population distribution obtained by SPOS on two cerium oxide type slurries. These slurries are known to be problematic in terms of stability and tend to have significant populations of large particles. Slurry 1 was known to be a well performing slurry while Slurry 2 was observed to produce sediment at the bottom of its container and was thought to be unstable. These slurries were specified by the manufacturer to have a mean diameter of 350 nm. These distributions begin at 1 micron. As expected, the PSDs resemble smoothly decaying tails. The tail for Slurry 2 is noticeably broader than the tail of the more stable Slurry 1. This correlates with greater tendency of slurry.
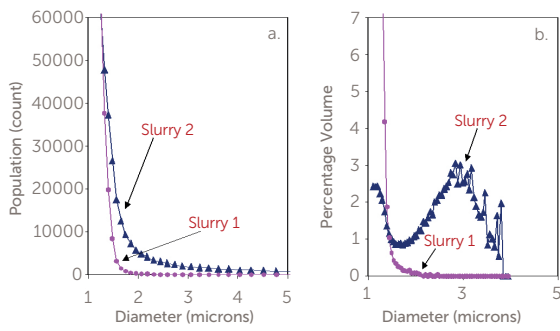
Figure 1. A. Population distribution of cerium oxide Slurry 1 (circles) and Slurry 2 (triangles); B. Volume weighted PSDs for Slurry 1 and Slurry 2.

Figure 2. Volume weighted PSDs of Slurries 1 (circles) and 2 (diamonds) obtained by LD. A. Index of refraction = 1.65 + 0.01i. B. Index of refraction = 1.65 + 0.10i

They emphasize the differences between the two samples more clearly. For Slurry 2, particles greater than 2 microns contribute relatively more of the solids volume. Furthermore, one can calculate from SPOS data the absolute percentage of the volume contributed by the particles in the tail. It was determined that for Slurry 1, particles greater than 1 micron contribute 0.25% versus 0.68% for Slurry 2. Again this data supports the observation that Slurry 2 is significantly more aggregated. It should be noted that while the total amount of material in the tail for each sample is small, the effect on slurry performance could be significant.

Figure 2 contains the volume weighted PSDs obtained by LD on the same two cerium oxide slurries. Recall that the user of such an instrument must enter the real and imaginary indices of refraction. Generally, the real index of refraction for most materials is known, but this is not so with the imaginary index of refraction. Figure 2a contains the results calculated with a real index of refraction of 1.65 and an imaginary index of refraction of 0.01i while the data in Figure 2b was calculated with an imaginary index of refraction of 0.10i. Both sets of data were calculated from the same scattered light pattern. In each calculation, the data indicates that Slurry 2 has a broader distribution than Slurry 1 with more big particles, as expected. But this data still illustrates the difficulty of obtaining accurate quantitative information from LD. First, the choice of the imaginary index of refraction effected a 10% shift in the mean diameter for Slurry 1 and greatly altered the shape of the distribution for Slurry 2. Second, the results from Slurry 2 indicate that the majority (>70%) of solids volume was contributed by particles greater than 1 micron. This just isn't possible, and it conflicts with the results from a gravimetric analysis as well as those from SPOS that determined the solids percentage from particles greater than 1 micron to be less than 1 percent in Slurry 2. This data demonstrates the point made above, choice of refractive index greatly affects results from laser diffraction.
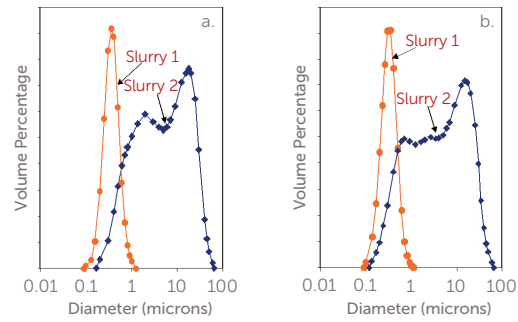
The next figure contains data that illustrates another problem with LD, its propensity to produce artifacts that do not represent true particle sizes. Figure 3 displays the volume weighted PSDs (ID=1.65 + 0.10i) of Slurry 1 after sonication. Recall that the PSD of the unsonicated sample (in Figure 2) consisted of a single peak with a relatively narrow width. After sonication for 20 seconds with an immersible sonic probe, the mean shifts higher and a second peak appears at 35 microns which contains 50% of the solids volume. Alone, this data suggests that sonication causes the slurry to aggregate. This is in contrast to the expected behavior. Sonication is expected to break up weakly bonded aggregates.
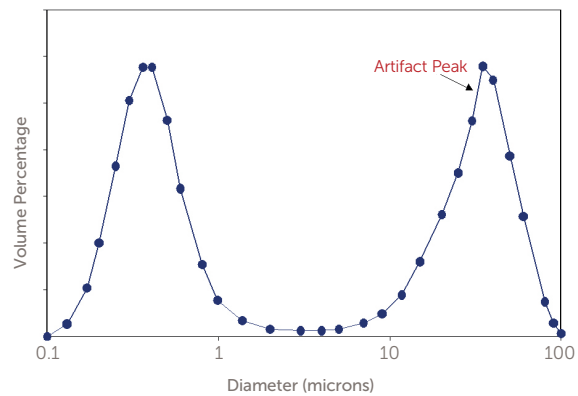

Figure 3. Volume weighted PSD of cerium oxide Slurry 1 after 20 seconds of sonication obtained from LD.

Figure 4a contains the number weighted PSD obtained from the same sample by SPOS. Again, only a tail is observed and no indication of a second peak at 35 microns is seen. Comparing the percentage solids in the tail for particles greater than 1 micron (0.23%) indicates no change from the unsonicated sample (0.25%). Figure 4b shows volume weighted SPOS data from Slurry 2 after sonication. It is superimposed with the unsonicated data from Figure 1. It is obvious that

the volume contribution for particles greater than 2 microns is considerably reduced due to sonication. The percentage volume contributed by the tail fell to 0.03%. SPOS seems to indicate that sonication had the expected effect of reducing large particles not creating them, in contrast to the LD results. It is obvious that the SPOS results are more physically realistic. One can only conclude that the PSD in Figure 3 resulted from mathematical artifacts produced by the inversion of the scattered light pattern. This again demonstrates the hazards of using LD to predict slurry performance.

greater than 5 microns. Figure 5b contains a volume weighted PSD (ID = 1.08 + 0.10i) obtained by LD on Slurry A. The PSD for Slurry B was identical. As can be seen, it consists of a single, symmetrical peak centered at 0.15 microns but with no particles greater than 1 micron. This is a reasonable light scattering result, and it shows that useful mean diameter information can be obtained by LD when the sample has a narrow PSD. On the other hand, this figure demonstrates again the lack of sensitivity of LD. While SPOS was able to see differences in these two silica slurries, LD could not.
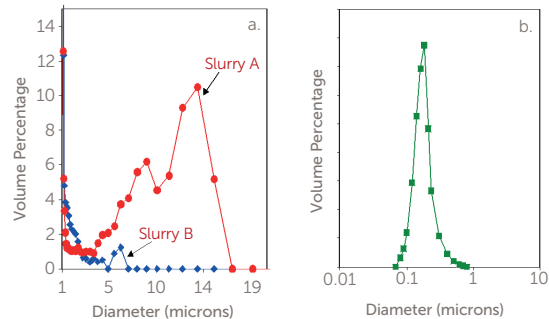

Figure 4. A. Slurry 1 after 20 seconds of sonication; B. Slurry 2 before and after sonication.

Figure 5. A. Volume weighted PSDs for silica Slurry A and B obtained from SPOS. B. Volume weighted PSD for silica Slurry A obtained from LD.

As one further example, consider the data found in Figure 5. This data was obtained from a silica based CMP, more commonly used than the cerium oxide slurries. Figure 5a contains the SPOS tail data (volume weighted) of two silica slurries, beginning at 0.5 microns. Figure 5a contains the SPOS tail data (volume weighted) of two silica slurries, beginning at 0.5 microns. The mean diameter of these slurries is thought to be in the 0.10 to 0.15 microns range. As can be seen, Slurry A has a significant volume contribution made by particles in the 2 – 20 micron range while Slurry B has no particles

Hopefully this data, as well as that in the previously discussed figures illustrates the importance of quantifying the large outlier particles that when present in CMP slurries can cause defects and lower chip yields. At a time of falling processor prices, maximizing the yield even by small amounts can have significant economic returns. The only technology available that can do this accurately is SPOS.

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