

Understanding & Controlling Large Particle Counts (LPC) in Chemical-Mechanical Planarization (CMP)

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EXECUTIVE SUMMARY

While it has always been important to control Large Particle Counts (LPC) in CMP processes, this key process control metric has become even more important for new materials and applications. Commercially available slurries today show very low LPC levels as delivered, yet improper process conditions can create LPC due to residues as well as slurry agglomeration. Thus, data taken from as-delivered slurries are not reliable predictors of final defect counts. Tools allow for the early detection of LPC excursions, and proper process recipes and consumables sets can be optimized to prevent LPC formation. Fumed silica slurry LPC >0.469µm in diameter can be detected with dual-sensor SPOS, and binned using field-flow fractionation (FFF).

As CMP is used in new integration flows, there can be new challenges in the specifications for surface cleanliness and defectivity. For IC fabs, transistor gate processing requires extremely low defectivity levels, and a large scratch is likely to kill a transistor. New IC interconnect dielectric materials generally use ever thinner barrier layers that are more sensitive to defects. Re-working a complex IC structure built with mere monolayers of thin-films may be impossible or prohibitively expensive, so preventing defects associated with CMP is even more important than in the past.

Planarization processes continue to play critical roles in modern micro- and nano-device processing. Whether enhanced planarity to compensate for lithographic depth-of-focus limitations in 45nm and 32nm node IC manufacturing, or new materials for crystal-stacking and wafer-level packaging (WLP) to enable true 3D ICs and MEMS, chemical-mechanical planarization (CMP) remains central to microelectronics manufacturing [1].

The overall trend is that more and more device layers in the fab as well as more and more wafer-level packaging flows require CMP steps for overall process integration. From high-k metal-gate (HKMG) CMOS transistors for 45nm and beyond, to through-silicon vias (TSV) for heterogeneous 3D integration, cleverly engineered substrates such as stressed-silicon-on-insulator (sSOI) and silicon-on-diamond (SOD) all require properly tuned slurry chemistries and process recipes.

TSV for 3D integration are under development in many different variations, including the use of poly-silicon (poly), tungsten (W), and copper (Cu) as embedded electrical conductors. They all require dielectric isolation from the silicon substrate, so some manner of chemical-vapor-deposition (CVD) oxide or nitride and/or spin-on-polymer (SOP) is typically exposed along with the conductor during a CMP step. Tuning the slurry chemistry selectivities to the conductor, insulator, and silicon allows for some degree of surface engineering. Large scratches can short TSV, and also can ruin the hermeticity that some 3D WLP require from Cu-Cu bonding.

Since slurries are composed of small particles, proper analytical screening techniques are required to predict the defect creation potential of CMP slurries. It has been shown that large scratch defects post-CMP can be traced to large particle counts (LPC) in CMP tools [2,3]. The LPC is an estimate of the number (or mass) of particles present in the large particle tail of the slurry's particle size distribution [4,5].

Data taken from as-delivered slurry provide reasonable incoming quality control (IQ) checks, and are necessary for process control. However, while necessary, these data are not sufficient to predict the defect results post-CMP, since non-optimal process parameters often result in the formation of large particles by agglomeration. Consequently, before we can control LPC we must first understand their origins.

UNDERSTANDING LPC SOURCES IN MODERN CMP

In CMP systems, slurry stability is qualitatively assessed through interparticle force or zeta potential measurements. However, these types of measurements do not fully describe agglomeration phenomena in CMP slurries. The presence of agglomerated particles in a CMP slurry is one of the main causes of defects during polishing, particularly as the manufacturing nodes continue to scale down.

Therefore, a new experimental/theoretical approach is needed to quantify the degree of agglomeration in CMP slurries. One approach involves subjecting the slurry to high-shear forces and measuring agglomeration as LPC in the tail distribution [6]. Slow coagulation occurs due to collisions that have enough energy to overcome the electrostatic repulsion between particles. By modeling changes in LPC using Smoluchowski's slow aggregation theory [7,8], we can quantify the degree of agglomeration caused by external shear stress and internal slurry chemistry.

The Smoluchowski theory assumes that the particle collisions are due to Brownian motion, and are proportional to the square of the particle concentration. During slurry delivery, the shear flow causes particles to approach each other, and when the attractive Van der Waals force is greater than the repulsive interparticle force, then particle agglomeration occurs. The degree of particle agglomeration that occurs is determined by slurry properties such as interparticle forces, external shear stresses from pumps, and the number of turnovers of the slurry.

In a prior report [6], Cu CMP slurry based on 80nm silica particles was used to polish silicon wafers covered with a blanket Cu film. As deposited, the Cu film roughness was 6.14 nm (rms), while as-received slurries resulted in 2.64 nm (rms) post-CMP surface roughness. For this CMP sys-

tem, low pH chemistry tends to induce LPC formation, while high pH allows particles to retain sufficient repulsive forces to prevent agglomeration. Thus, as-circulated slurries at pH 3 had more agglomerated particles, which resulted in 7.98 nm (rms) surface roughness and large microscratches; however, circulated slurries at pH 9 resulted in just 2.99 nm (rms) roughness (Fig. 1).

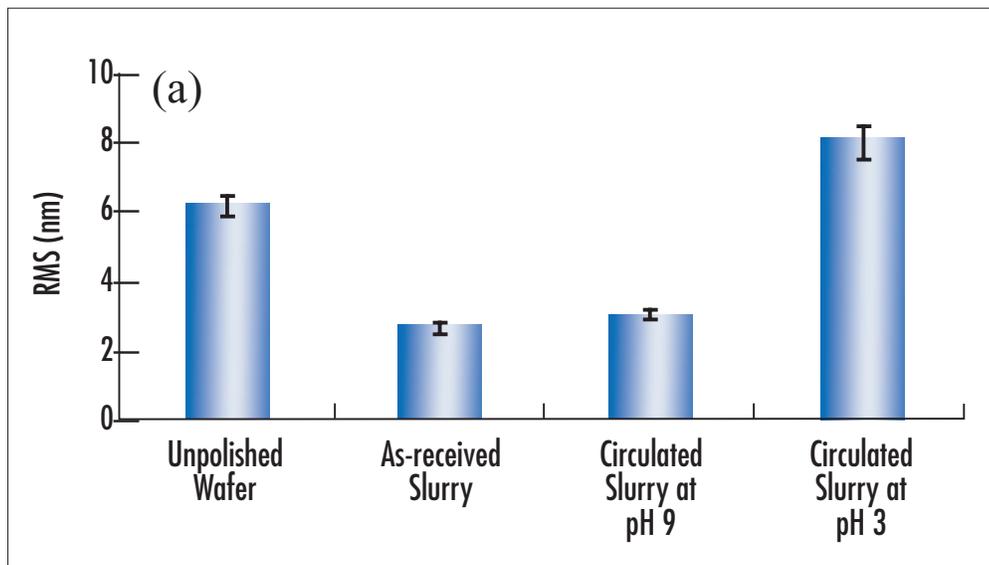


Figure 1. Surface roughness (rms) of Cu films pre- and post-CMP under various conditions, showing high pH induces particle agglomeration that causes roughness and defects [source: Ref.6].

In CMP of both dielectrics and metals, pumps within the slurry distribution system can play a significant role in increasing both the number and distribution of oversized particles. The effect of stress induced by different types of pumps on particle agglomeration has been investigated [9]. The size of the particles in circulated silica slurries and the surface roughness of low-k samples were characterized using a single-particle optical sensor (SPOS) and atomic force microscope (AFM), respectively.

Lower agglomeration of particles during slurry handling by a magnetically levitated centrifugal pump occurred because of its contact-free impeller in the pump housing, which provided a smooth pulseless and low-shear flow. The positive displacement pump generated highly localized shear stresses near the wall during the pump stroke, resulting in a significant increase in oversized particles. The mean value of normalized oversized concentrations in the positive displacement pump system at 500 turnovers was found to be 6 times higher than that of a magnetically levitated centrifugal pump, due to approximately 100 times higher shear stresses. Low-k wafers polished by circulated slurries from the magnetically levitated centrifugal pump system showed little increase in surface roughness and defectivity.

Other researchers have shown that agglomerated slurry particles remain intact during distribution, such that they can induce defects [10]. Model predictions were compared to experimental copper CMP data. The model was unable to predict the material removal rate (MRR) when the slurry did not have any chemical additives because the dispersion was unstable and small fluctuations in the agglomerate size and distribution caused large changes in the predicted MRR. With proper chemical additives for stability, modern slurry particles should not significantly agglomerate.

However, even if the slurry particles themselves do not agglomerate, the byproducts of the CMP process may form LPC. Since CMP inherently involves the removal of surface asperities with abrasive particles and polishing processes, it leads to nanoparticles released into the solution. The diffusion-limited agglomeration (DLA) of Cu-containing nanoparticles has been modeled [11], with the conclusion that Cu nano-agglomerates can rapidly grow to large sizes.

RESOLVING LARGE PARTICLES IN SLURRIES

There is no general agreement on the specific range of particle sizes that represent the LPC, but a diameter of $0.5\mu\text{m}$ is typically cited as its minimum size limit [12,13]. A variety of particle size distribution analysis techniques, such as static light scattering, [13,14,15] sedimentation analysis [13], capillary hydro-dynamic fractionation (CHDF) [12], and acoustic spectroscopy [12,13,16] have been applied to quantify the LPC in CMP slurries. However, these methods generally suffer from a lack of analytical sensitivity required for the accurate characterization of the LPC corresponding to trace sub-ppm levels of large particles.

Single-particle optical sensing (SPOS) exhibits the high sensitivity required to quantify the fraction of slurry particles constituting the large particle count of a CMP slurry [12,13,17-21] but few strong correlations between SPOS-derived LPC measurements and surface defect counts have been reported [21,22].

A SPOS technique incorporating dual optical sensors [22] has been employed in the analysis of particle size distributions and the LPC of fumed silica CMP slurries. The dual-sensor SPOS method measures the contribution to the LPC and the particle size distribution from

particles smaller in size than the particles normally measured with established SPOS techniques. This new approach is demonstrated in concert with the CMP of dielectric surfaces.

The LPC for particles in fumed silica CMP slurries with silica sphere-equivalent diameters greater than $0.469\mu\text{m}$ was provided by dual-sensor SPOS measurements. A model AD-10300-001 SPOS instrument (Celerity Inc., Tualatin, OR), equipped with model LiQuilaz S03 and LiQuilaz S05 particle sensors (Particle Measurement Systems Inc., Boulder, CO) was employed. Particle size distributions for the slurries were characterized by static light scattering (model LA-910, Horiba Instruments Co., Irvine, CA) and capillary hydrodynamic fractionation (model CHDF2000, Matec Applied Sciences Inc., Northborough, MA).



CMP conducted under clean room conditions employed an IPEC 472 polisher (Novellus Systems Inc., San Jose, CA) equipped with an A100 polishing pad (Cabot Microelectronics Corp. Aurora, IL). The wafers used were 200mm diameter bulk silicon coated with blanket PECVD (TEOS-precursor) silicon oxide (SEMATECH, Austin, TX) layer thickness of $\sim 800\text{nm}$. Post-CMP, the wafers were dipped in dilute hydrofluoric acid (HF) to decorate any defects. Scratch defects were counted using a model Surfscan SP1TBI system (KLA-Tencor Inc., San Jose, CA) operated in DCO mode. The morphology of surface scratch defects was characterized by low-voltage scanning electron microscopy using a model eV300 scanning electron microscope (KLA-Tencor Inc., San Jose, CA).

Correlations Between Measurement Techniques

The results of scratch counts vs. LPC correlation suggest that further extension of the dual-sensor SPOS technique to even smaller diameter particles is possible through the incorporation of a third sensor into the SPOS system. This system would be capable of detecting and counting particles with polystyrene latex bead (PLB) equivalent light-scattering diameters as small as $0.22\mu\text{m}$. For silica spheres this lower size limit corresponds to $0.36\mu\text{m}$, as determined by extrapolation of the data.

The ability to extend SPOS analysis to smaller diameters provides an opportunity to bridge the gap between the analytical ranges of SPOS and CHDF or static light scattering and affords an accurate particle size distribution analysis

for fumed silica slurries over a composite diameter range of $<0.1\mu\text{m}$ to $>2\mu\text{m}$. This would presumably permit the mapping of the entire particle size distribution, allowing the relationship of the size and shape of the tail of the distribution to be studied in light of the size and shape of the main body of the distribution.

This wide range of accurate particle size distribution analysis holds the promise of better characterizations of CMP processes for which particle size is a determining factor, such as the dependence of removal rate on the diameter distribution of the slurry's abrasive particles [16,23].

Static light scattering and CHDF analyses of $1\text{-}\mu\text{m}$ -filtered slurries, an unfiltered slurry containing particles greater than $1\mu\text{m}$ in diameter, and model mixtures of these slurries measured 98% of the particle size distributions. However, these methods could not detect particles with diameters as small as $0.4\mu\text{m}$. Dual-sensor SPOS can readily detect and count particles in slurries with diameters greater than or equal to $0.5\mu\text{m}$, i.e., the LPC. Calculations of the Mie scattering efficiency for PLB and for silica spheres allowed the LPC for the slurries to be expressed on a silica sphere-equivalent, light-scattering diameter basis (Fig. 2).

This size scale transformation also enables the direct comparison of silica slurry particle diameter distributions evaluated by static light scattering and CHDF.

Correlations between LPC and scratch counts on SiO_2 films, obtained under a defined set of tabletop polishing conditions, indicate that the fraction of large particles with estimated diameters greater than $0.68\mu\text{m}$ contribute more effectively to scratch count generation than smaller particles. The counting of these particles produced a twofold increase in scratch forming particles included in the correlation relative to the correlation based on LPC measurements by single-sensor SPOS.

The correlation obtained for silica particles greater than $0.68\mu\text{m}$ in diameter is limited as a predictor of scratch counts on the basis of the measured LPC due to significant experimental uncertainty in the measurement of both scratch counts and LPC. A statistically significant difference in predicted scratch counts at the 95% confidence level between two slurries corresponded to a minimum difference in LPC of 1.8×10^5 particles/ g_{slurry} .

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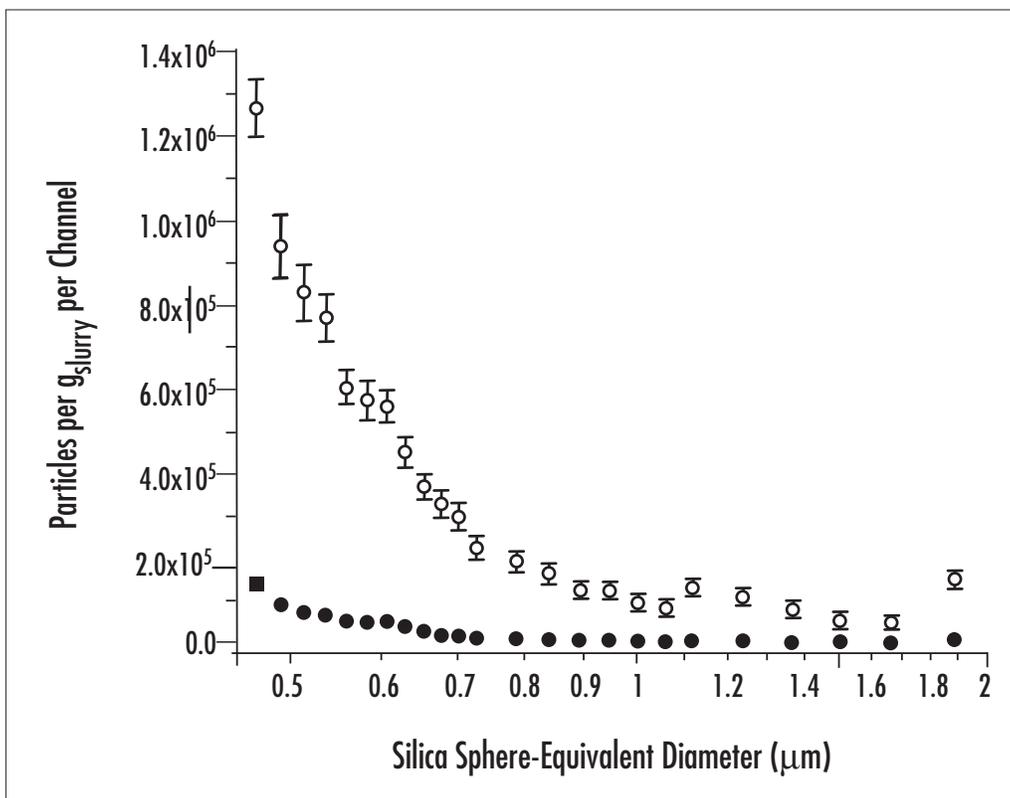


Figure 2. Particles per gram of slurry per channel and measurement error bars versus silica sphere-equivalent diameter for slurry A (solid circles), slurry B (open circles).

LPC SILICA SPHERE CALIBRATION

To obtain the most accurate results in modeling and detecting LPC in fumed silica slurries, it is important to use silica particles instead of the somewhat customary polystyrene latex beads (PLB) as standard reference particles. Because the scattering efficiency of a silica sphere is significantly less than that of a PLB, equivalent Mie scattering intensity for these materials will only be attained when the silica sphere is significantly larger in diameter than the polystyrene sphere. For example, diameters of 0.5 μm and 1.0 μm for a PLB produce equivalent Mie scattering intensities as 0.735 μm and 1.846 μm silica spheres, respectively (Fig. 3).

Application of silica sphere-equivalent light scattering diameters in the dual-sensor SPOS analysis of the fumed silica slurries allowed the particles per gram of slurry per sensor channel to be measured over a diameter range of 0.469 μm to 20 μm . Figure 4 shows representative results for a 1 μm -filtered slurry (slurry A) and a known bad, unfiltered slurry (slurry B). The determination of silica sphere-equivalent, light scattering diameters also allowed dual-sensor SPOS results to be compared on the same size scale used for particle size distribution evaluations by static light scattering. Scratch morphologies, determined by SEM, were dominated by oxide chatter scratches. This finding is in agreement with previously described SEM studies of oxide polishing [24].

The use of silica sphere-equivalent light scattering diameters as the basis for the dual-sensor SPOS analysis allowed for the inclusion of smaller diameter particles in the measurement of LPC. Transformation of the PLB-equivalent, light scattering diameters into a silica sphere-equivalent, light scattering diameter scale also allowed for the direct comparison of static light scattering, CHDF and SPOS data on a common, silica-based diameter scale. The dual-sensor SPOS methodology further enhanced the direct comparison of findings from multiple techniques by minimizing the gap between the measured silica size ranges for SPOS and the other particle sizing methods. Detection and counting of smaller silica particles via dual-sensor SPOS also provided a 14-fold lower minimum detection limit for the silica particles defining the LPC relative to that obtained from a single SPOS sensor [22].

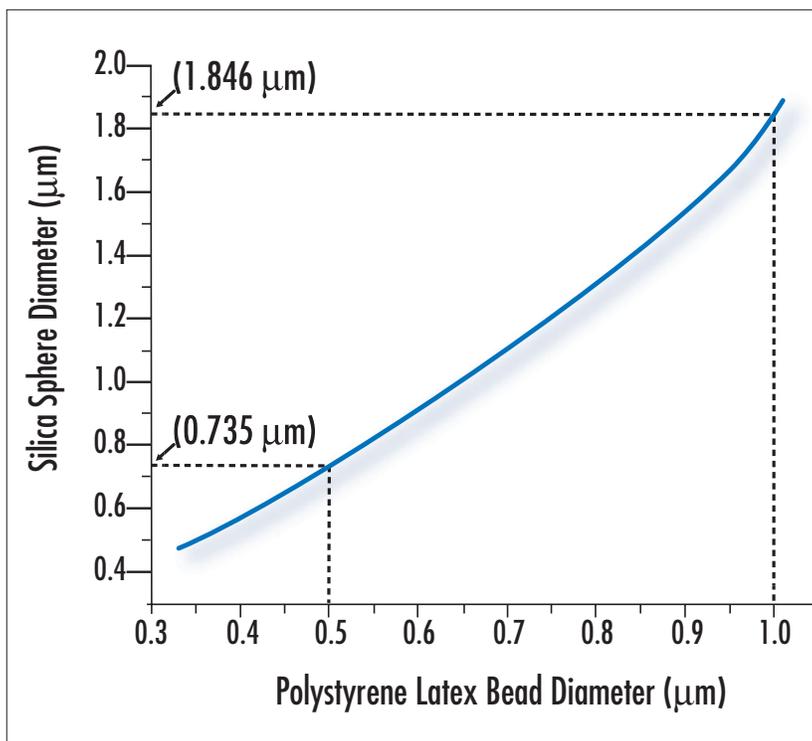


Figure 3. Graph of polystyrene latex bead (PLB) and silica sphere diameters that produce equivalent Mie scattering intensities using the Celerity/PMS SPOS sensors (solid line). Representative particle diameter pairs are marked by dashed lines indicating the diameters of silica spheres that produce equivalent Mie scattering intensity as 0.5 and 1.0 μm PLB.

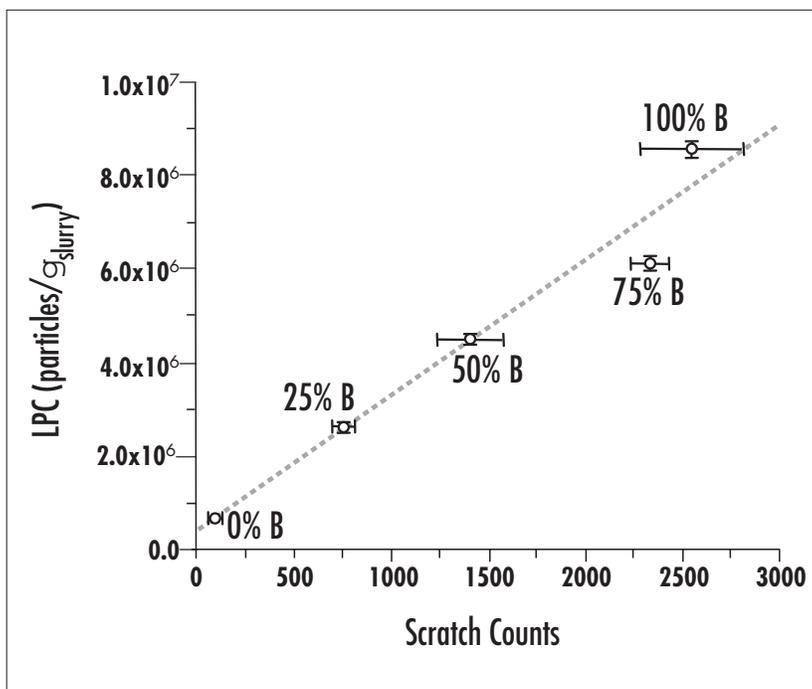


Figure 4. Correlation of LPC with Surfscan SP1TBI measured DCO scratch counts for clean room polished wafers as a function of wt% slurry B (known contaminated) in slurry mixtures. Error bars correspond to 1 standard deviation.

LPC BINNING USING FFF

However, the chemical and structural nature of these particles can not be determined from SPOS measurements [25,19] commonly used to determine the LPC. This lack of detail prevents the assignment of specific large particle types in the LPC as micro-scratch generators. In addition, a relative ranking of the micro-scratching potential for the different large particle types is also beyond the reach of conventional SPOS techniques.

Findings reported in a previous study for model particle mixtures indicate that a new method combining size separation of particles via flow field-flow fractionation (FFF) [26] and particle detection using dual-sensor SPOS can be applied in the detailed analysis of LPC in CMP slurries [27].

The FFF separation utilizes laminar flow conditions to induce a parabolic flow profile with its characteristic maximum flow rate at the center of the channel and decreasing flow velocities towards the channel walls. The FFF process commences with the transport of particulate

sample to a membrane accumulation wall by a crossflow of fluid (**Fig. 5a**). Since the closest distance of approach to the wall is limited to one particle radius, small particles will have a center of mass that is closer to the wall than large particles and will be transported to the detector at a lower flow velocity. Consequently, small particles elute later than large particles in steric mode FFF [28].

As previously reported [27], a particle sizing and counting method based on the coupling of FFF with dual-sensor SPOS detection was accomplished by means of a dilution interface that preserved the resolution of FFF-separated particles (**Fig. 5b**). Analysis of a model mixture of PLB of different diameters established that the FFF-SPOS system can resolve particles into discrete peaks for subsequent particle counting. Application of this method for the analysis of a colloidal silica standard demonstrated its use for materials commonly employed as CMP abrasives. Further development and refinement of the technique will enable compositional and structural analyses of heterogeneous large particle populations constituting commercial CMP slurries.

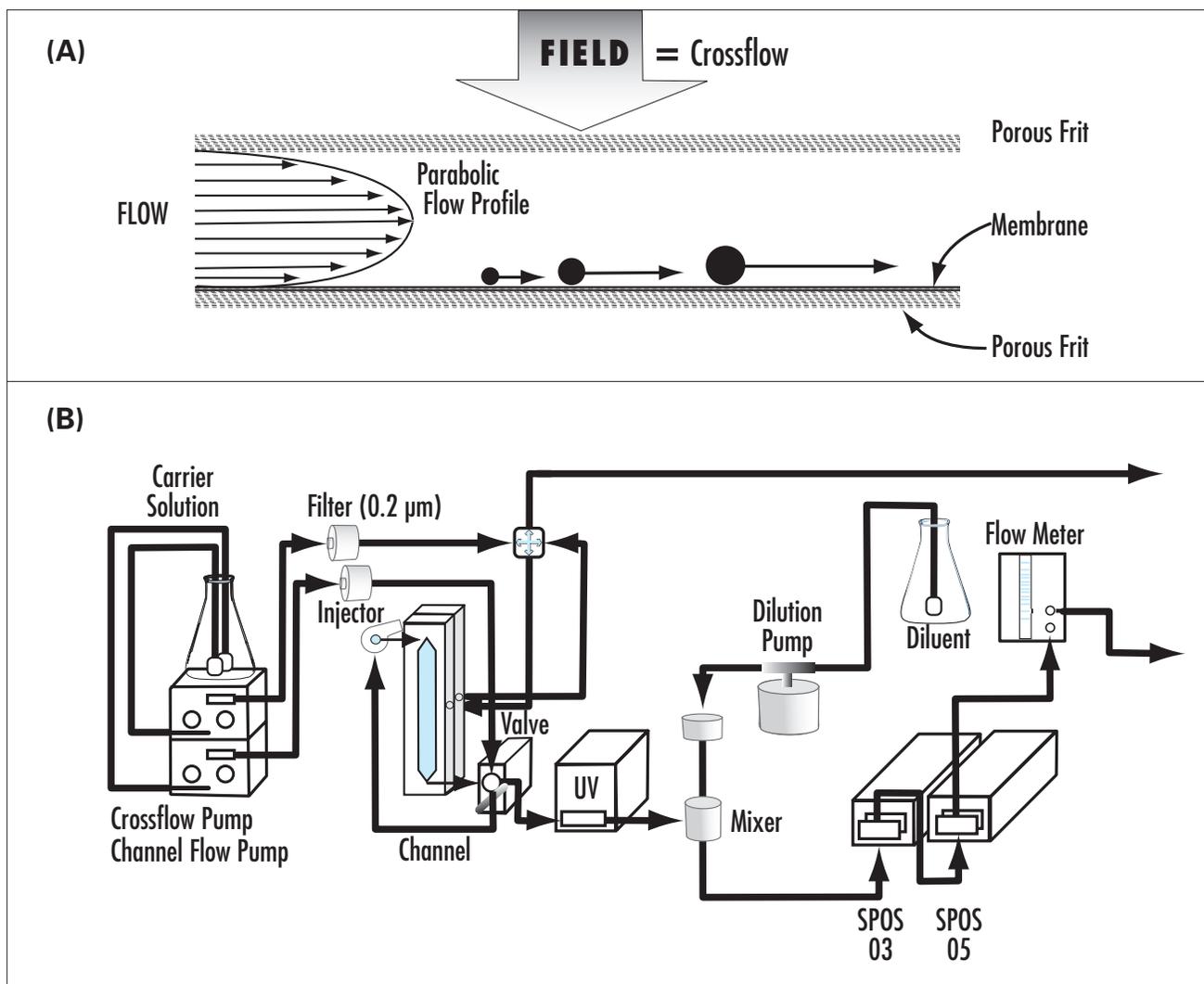


Figure 5. Schematic illustration of (A) steric mode flow FFF separation mechanism and (B) the FFF-SPOS system.

The large particle count (LPC) of as-delivered CMP slurry correlates poorly with post-CMP wafer defects in modern planarization systems. While LPC from the as-delivered slurry may have been significant in the past, the current state-of-the-art in creating CMP slurries ensures that LPC are minimal and in control. Also, today's CMP slurries are thoroughly engineered to ensure that chemical potentials tend to prevent the agglomeration responsible for most LPC in systems today.

Numerous polishing experiments revealed that slurries with more agglomerated particles due to the handling process caused more surface defectivity during polishing. Stressing the CMP system through circulating the slurry and/or changing a chemistry parameter such as pH can thus determine slurry stability and predict the particle-induced defectivity during CMP.

Still, LPC excursions can occur in CMP systems. Older pumping technologies may induce excessive shear forces that can induce agglomeration of both slurry particles and process byproducts. Cu nano-particles have been shown to agglomerate into LPC under the wrong conditions. Prevention is certainly the solution, and understanding the complex interactions between the wafer and the system is essential.

Dual-sensor single particle optical sensing (SPOS) can readily detect and count large particles in fumed silica CMP slurries. Static light scattering and capillary hydrodynamic fractionation could not detect slurry particles with diameters $> 0.5\mu\text{m}$ in these slurries. Silica

CONCLUSIONS

sphere-equivalent light scattering diameters were employed as the size scale basis in SPOS measurements, and allowed SPOS results to be directly compared with measurements obtained with other particle sizing techniques. When expressed on a silica sphere-equivalent light scattering diameter size basis, a minimum detected particle size of $0.469\mu\text{m}$ for the LPC analysis was established.



Analyses of mixtures of polystyrene latex bead (PLB) standards demonstrated conclusively that a flow field-flow fractionation (FFF) separation can be successfully interfaced with dual-sensor SPOS detection. Operation of the FFF-SPOS system in a steric FFF separation mode allowed the detection and quantification of PLB ranging in diameter from 0.3 to $3\mu\text{m}$. Using the multi-channel capability of the SPOS sensors, FFF-separated mixtures of PLB of different diameters can be resolved into discrete peaks corresponding to the individual standards in the mixture. Successful extension of the technique to the analysis of colloidal silica confirmed that materials

characteristic of the abrasives used in CMP slurries can be analyzed via FFF-SPOS.

These techniques may be part of a comprehensive defect reduction and prevention strategy for both metal and dielectric CMP. We are still a long way away from the ultimate goal of a production technique capable of providing a quantitative Pareto chart of LPC in real systems. However, our qualitative results are encouraging, and our models already provide significant insights into excursion mechanisms.

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