How Pump-Induced Particles Affect Low-k CMP Defectivity

High shear flow generated by positive displacement pumps increases the distribution of oversized particles, leading to significantly increased wafer surface defectivity (scratches or roughness) during CMP, whereas less defectivity was found in slurries circulated by a magnetically levitated (maglev) centrifugal pump.

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Oversized particles in chemical mechanical planarization (CMP) slurries are one of the most important causes of defectivity during CMP of dielectrics and metals. The slurry distribution systems and pumps may play significant roles in increasing the number and distribution of oversized particles. We examined the stress effects and resulting wafer-level defectivity caused by positive displacement pumps and centrifugal pumps during low-k polishing. Excellent correlation between the pump-induced agglomeration effects and defectivity was established. Modeling and testing showed that the average shear stress in a positive displacement pump is ~100× higher than that of a magnetically levitated (maglev) centrifugal pump.

Particle agglomeration under shear flow

CMP slurries that consist of particles and chemicals could be the most critical consumable in the semiconductor industry[1,2]; however, some studies have shown that positive displacement pumps (e.g., bellows and a diaphragm) may generate high shear stress and tend to agglomerate particles during slurry handling.[3-6] Aggregated particles in the slurries not only could reduce the lifetime of filters,[7] but could also cause surface defectivity during the CMP process.[8,9] We must understand the mechanism of pump-induced particle agglomeration to solve this problem.

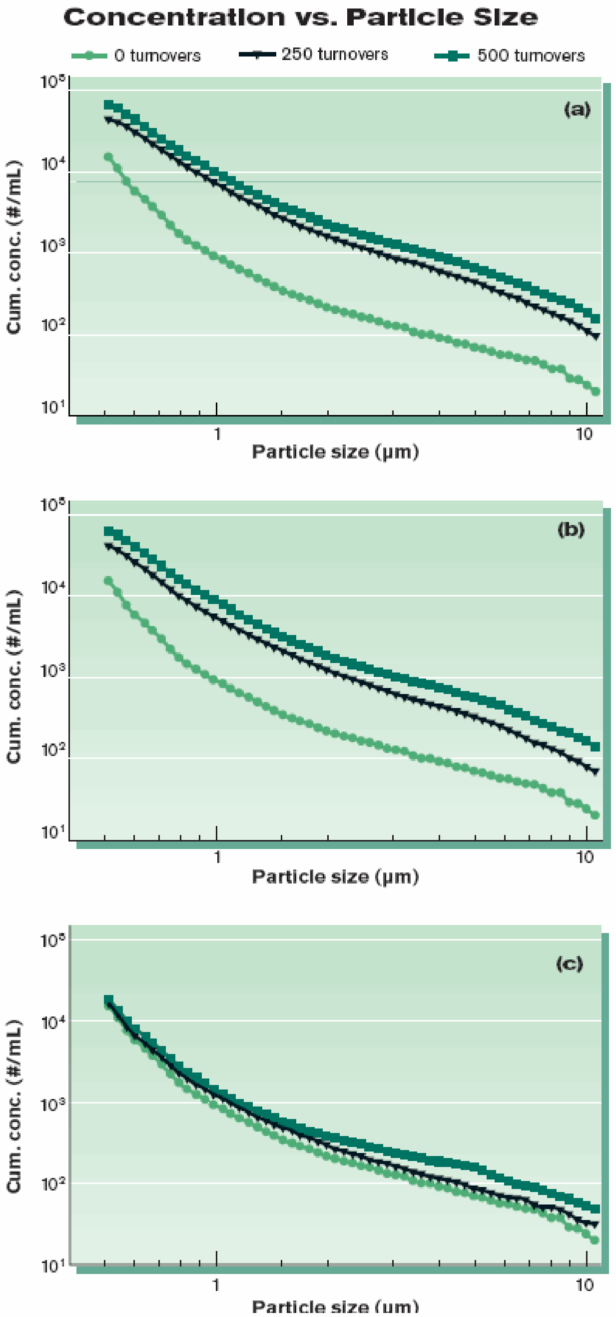
The kinetic theory of rapid aggregation was first worked by von Smoluchowski.[10] His kinetic model assumes that the particle collisions are binary and proportional to particle concentration. The aggregation rate of k-fold aggregates, *dNk*/*dt*, is given by the time evolution of the cluster size aggregates, *i* and *j*-folds:

$$\frac{dN_k}{dt} = \frac{1}{2}\sum_{i+j=k}^{i=k-1} k_{ij} N_i N_j - N_k \sum_{k=1}^{\infty} k_{ki} N_i \qquad (1)$$

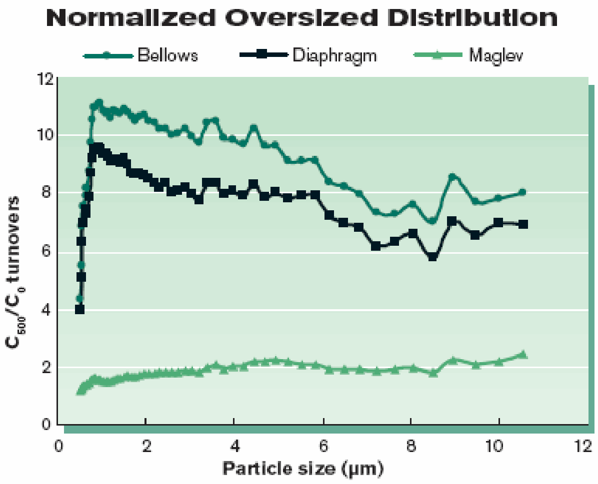
where k_{ij} is the second-order aggregation constant. In this study, high shear flow generated by pumps could be the main cause of particle agglomeration in the slurry delivery. We used the Smoluchowski theory of shear aggregation[10,11] to simulate the process of particle aggregation under shear flow. The aggregation constant, k_{ij}, is a function of shear rate, G, and particle size, a:

$$k_{ij} = \frac{4}{3} G (a_i + a_j) \qquad (2)$$

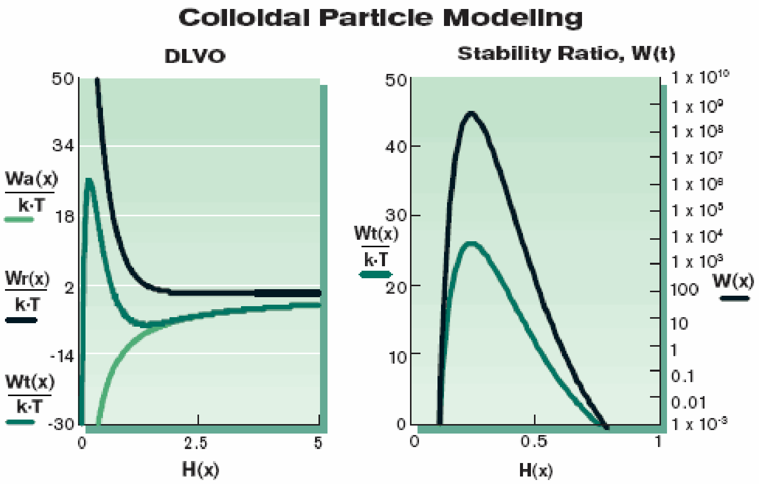
If we consider the effect of electrostatic interaction between particles in the system, the total electrostatic interaction may provide a potential



1. The maglev centrifugal pump (c) caused less agglomeration than the bellows (a) or diaphragm pump (b) because of insignificant change in particle tail.



2. The normalized oversized particle distributions, a ratio of circulated slurries to uncirculated slurry, determines the stress effect on particle agglomeration.



3. When modeling shear force and the aggregation of particles, attractive and repulsive electrostatic interactions are modeled in the DLVO theory and the stability ratio of silica slurry, shown at pH 10.

barrier to hinder particle agglomeration and reduce the aggregation rate, which is called slow aggregation. The rate of k-fold aggregates can be revised by introducing the stability ratio (*W*), which is the ratio of rapid aggregation rate to the slow aggregation ratio. The aggregation rate can be expressed as:

$$\frac{dN_k}{dt}=\frac{1}{2}\sum_{i+j=k}^{i=k-1}(k_{ij}/W_{ij})N_iN_j-N_k\sum_{k=1}^{\infty}(k_{ki}/W_{ki})N_i \qquad (3)$$

W could be determined by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory,[12] which states that the stability of colloidal particles depends on a balance of attractive Van der Waals forces and repulsive double layer forces:

$$\tau=\frac{W}{k_g N_0} \qquad (4)$$

where $1/\kappa$ is the electrical double layer, V_{max} is the maximum of interaction energy, which can be obtained from the total potential energy, expressed as the sum of repulsive (V_R) and attractive (V_A) potential:

$$W=\frac{1}{2\kappa a}\exp\left(\frac{V_{max}}{kT}\right) \qquad (5)$$

Furthermore, the individual aggregates (e.g., singlets, doublets and k aggregates) are derived from Equation 3.

$$V_{tot}=V_A+V_R \qquad (6)$$

$$N_1=\frac{N_0}{(1+t/\tau)^2} \qquad (7)$$

$$N_2=\frac{N_0(t/\tau)}{(1+t/\tau)^3} \qquad (8)$$

$$N_k=\frac{N_0(t/\tau)^{k-1}}{(1+t/\tau)^{k+1}} \qquad (9)$$

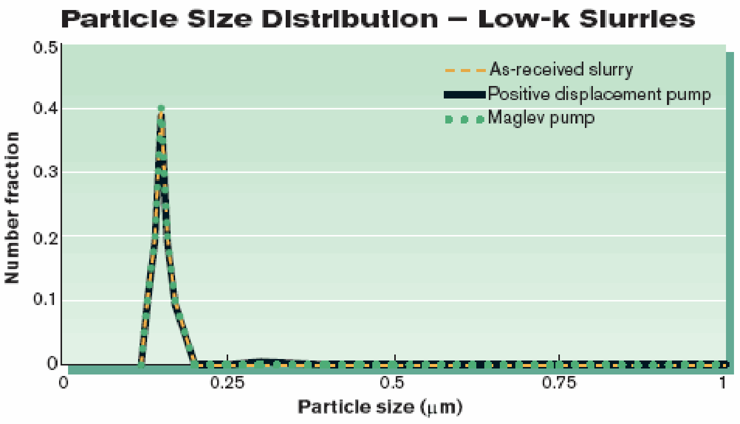
Importantly, the evolution of aggregate concentrations is determined by the nature of the particles (size and surface functionality), ionic strengths of the slurry, and external mechanical forces applied on the slurry itself during the slurry handling process.

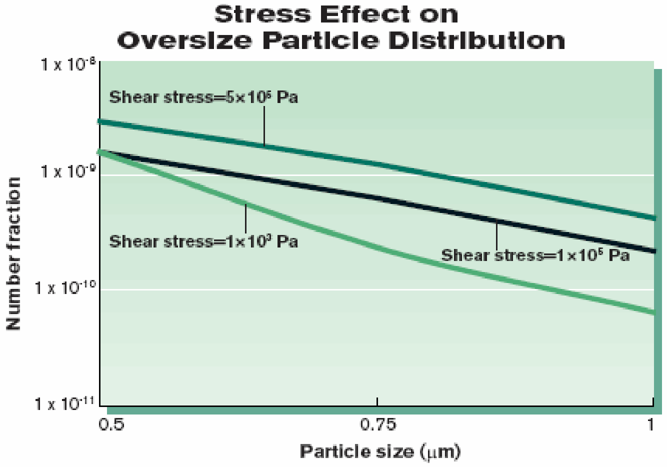
Defectivity of low-k CMP

Abrasive particles in the CMP slurry typically provide the mechanical component of the polishing process. Researchers have developed polishing models based on the interaction between particles and wafer surfaces. Cook[13] first proposed the indentation model for glass polishing, where indentation depth or material removal is determined by particle size, down pressure and material properties (e.g., elastic modulus and hardness). Basim[14] indicated that the presence of oversized particles in the slurry may vary the mechanism of polishing and increase surface defectivity during CMP. Her polishing model suggests that the indent volume or contact area is proportional to particle size and particle concentration in the slurry. Zeng[15] demonstrated a dynamic polishing model that considered the viscoelastic properties of pads and surface roughness of wafers. His transient modeling indicates that the polishing rate decreases with increasing particle size when the average particle size is larger than the optimum size.

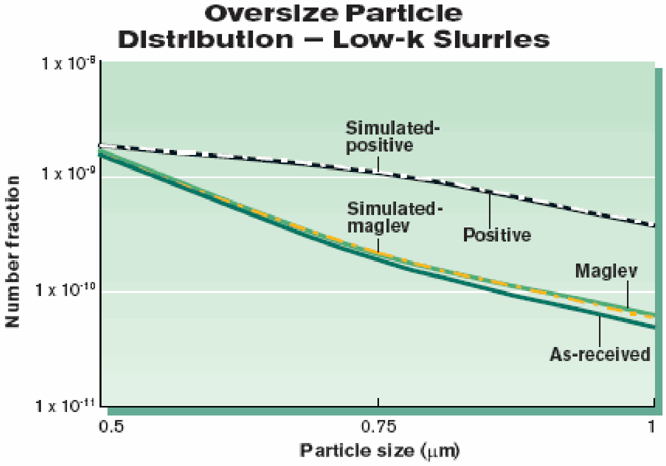
The introduction of more fragile low-k materials into semiconductor manufacturing increases the likelihood of surface defectivity during CMP.[16,17] To reduce/minimize process dependent defectivity, the particle size distribution,

4. Given the same slurry (150 nm silica), different pumps will have different effects on the particle size distribution. The most pronounced change is in tail distribution, which is shown in Fig. 1.




Stress Effect on Oversize Particle Distribution

5. Simulation shows that higher shear stress caused a significant increase in number fractions of oversize particle distribution.


Oversize Particle Distribution – Low-k Slurries

6. Comparison of experimental and simulated data of oversized particle distribution in low-k slurries. Data shows maglev pump has a much lower shear stress.

especially in the oversized tail region, should be as small as possible and should not increase with time during the slurry delivery and polishing process. However, high shear flow generated by pumps could significantly increase the oversized particles volume during slurry delivery.

Oversized particles can also increase mechanical stress on the wafer surface, leading to increased surface defectivity during the polishing. Although the industry is moving toward lower down-pressure CMP processes for copper and low-k, the stress effect on particle agglomeration can still result in considerable damage to metals and dielectrics.

Pumps, surface defectivity

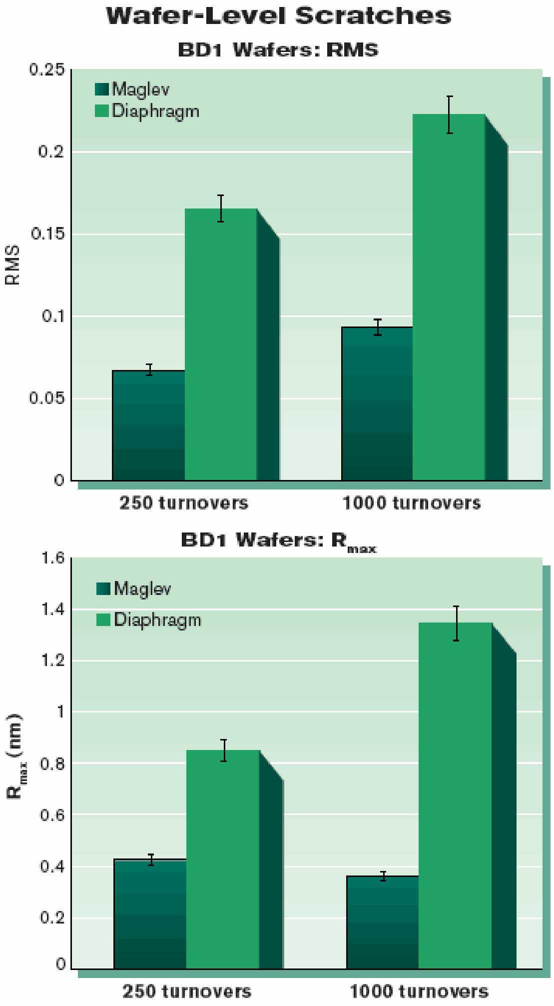
We designed a slurry delivery system to observe the effect of pump-induced particle agglomeration. It contains an air supply, 12-ft-long PFA tubing distribution loop, slurry tank, pressure gauge and flow meter. Positive displacement pumps (e.g., bellows or diaphragm pumps) and a maglev centrifugal pump were used to circulate a commercial low-k slurry. We held the flow rate of slurry constant (12 L/min) by fixing the gas pressure of the positive displacement pumps (30 psi) and centrifugal pump (5900 rpm). We observed the effect of pump-induced particle agglomeration at 250, 500 and 1000 turnovers.

Low-k slurries circulated by positive displacement and centrifugal pumps were used to polish Black Diamond 1 (BD1) low-k films (k=3.0) on 1 in. square pieces of wafers using Struers RotoPol-31 tabletop polisher. For each run we used a down pressure of 3 psi, polishing time of 1 min, slurry flow rate of 100 mL/min, and rotation speed of 150 rpm. The surface defectivity of low-k wafers was determined by atomic force microscope (AFM) with a Digital Instruments' Nanoscope III and an optical microscope to characterize surface roughness and defect density after polishing.

We observed the effect of pump-induced particle agglomeration using a AccuSizer 780 sensor, which determines the cumulative oversized particle tails and normalized oversized particle distributions. Figure 1 shows the cumulative distribution curve of oversized particles in low-k slurries circulated by both pumps at 0, 250 and 500 turnovers. These oversized particle tails increased with the number of turnovers and were influenced by pump type. The bellows and diaphragm pumps generated high shear flow in the slurry delivery and significantly increased the cumulative oversized particle tails during slurry handling. An insignificant increase in oversized particles was found in the case of the maglev pump. Furthermore, the normalized oversized particle distributions, a ratio of circulated slurries to uncirculated slurry, can obviously determine the stress effect on particle agglomeration (Fig. 2). Thus, a maglev centrifugal pump generated lower shear stress in the slurry delivery than the positive displacement pumps.

Correlation Data Between Normalized Oversized Particles and Surface Defectivity

Pumps (turnovers)/ flow rates (L/min)	Normalized oversized particle numbers	No. of scratches on BD1	Scratch density on BD1 (#/mm²)	RMS (nm)
Bellows (1000)/9	3.37	2.2	3.6	0.15
Maglev (1000)/9	1.51	0.3	0.5	0.07
Bellows (1000)/12	3.64	2.8	4.4	0.18
Diaphragm (250)/12	2.70	1.0	1.5	0.17
Diaphragm (1000)/12	3.10	2.1	3.4	0.22
Maglev (250)/12	1.07	0	0	0.07
Maglev (500)/12	1.20	0	0	0.06
Maglev (1000)/12	1.22	0.7	1.1	0.09



7. Surface defectivity in low-k CMP using circulated slurries from a diaphragm and centrifugal pumps.

Modeling particle agglomeration

Using the Smoluchowski theory of shear aggregation, this slow aggregation model describes the pump's effect on the evolution of individual aggregates. These aggregate concentrations are influenced by particle types, slurry formulations and external mechanical forces applied on the slurry itself during the slurry handling process. The extent of particle agglomeration depends on the interaction between shear stress and inter-particle forces. These forces play an important role to stabilize the suspensions and are determined by the DLVO theory. The total interaction (Wt) or *W* is given by the balance between the attractive potential (Wa) and repulsive potential (Wr), as shown in Figure 3. We could use the W to predict the efficiency of particle collision and simulate the stress effect on the growth of aggregate concentrations.

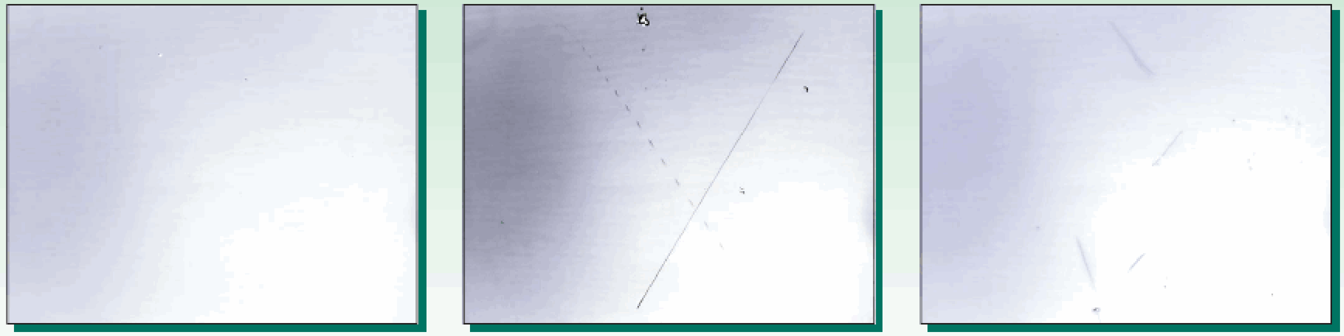
First, we simulated the pump's effect on particle agglomeration in low-k slurry to observe the evolution of particle size distributions after 500 turnover times. We took the input values for simulation, such as initial particle size distribution, slurry properties and electrostatic interaction, from the experimental data. Figure 4 shows the particle size distributions of as-received slurry and circulated slurries by pumps. The centrifugal and positive displacement pumps slightly influence the initial particle size distribution, which is not the main reason to increase oversized particles. The key factor to influence oversized particle distribution is its as-received oversized particles content, which collides together, increasing the distribution of oversized particles under the shear flow. Thus, we would like to discuss how shear stress influences the oversized particle distribution.

Figure 5 shows how shear stress (10^3, 10^5 and 5×10^5 Pa) influences oversized particle distribution in low-k slurries. High shear flow in the slurry caused the particles to approach each other more closely and agglomerate more oversized particles after 500 turnovers. Furthermore, the comparison between simulated data and experimental data can be used to determine the shear stress generated by the pumps (Fig. 6). The simulated data has excellent agreement with the experimental data.

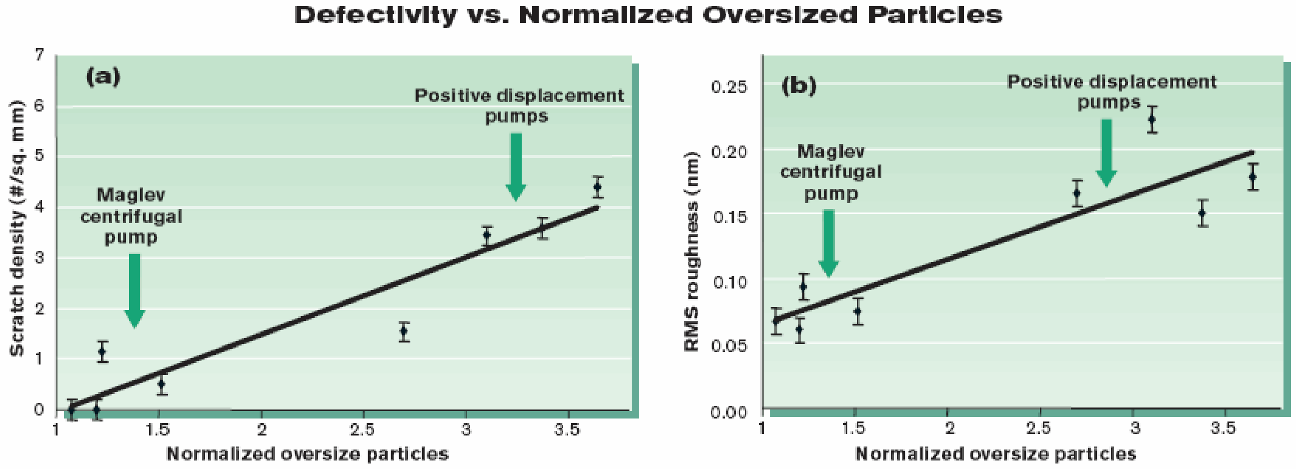
The simulation shows that the shear stress generated in positive displacement pumps is approximately two orders of magnitude higher than maglev pumps.

Wafer-level defectivity

Figure 7 compares the surface defectivity of low-k wafers as a function of turnovers for slurries circulated by positive displacement and centrifugal pumps. Oversized particle distribution increased with turnovers and caused increased surface defectivity during CMP. The slurries circulated by positive displacement pumps caused more oversized particles and polished defectivity on low-k wafers than centrifugal pump processed slurries. Thus, the effect of the pump-induced oversized particles on defectivity could be determined by correlation between oversized particles and defect density observed on low-k wafers via optical microscopy (200X). Surface defectivity of polished BD1 wafers showed that circulated slurries of positive displacement pumps caused more micro scratches than circulated slurries of centrifugal pump (Fig. 8). These correlated data (e.g., defect density,



8. Fewer scratches were seen using optical microscopy (200X) for BD1 wafers with low-k slurry delivered by centrifugal pump (a) vs. diaphragm (b) or bellows (c).



9. There is excellent correlation between the increase of normalized oversized particles with scratch density and root mean square (RMS) roughness.

root mean square (RMS) and normalized oversized particle numbers) were obtained by varying turnovers and flow rates (Table). Consequently, excellent correlations between the increase of normalized oversized particle with RMS roughness and the scratch density were established (Fig. 9). In both figures, points near the origin correspond to slurries circulated by centrifugal pumps that have less effect of pump-induced particle agglomeration and less defectivity during the polishing. Points far off from the origin correspond to slurries circulated by positive displacement pumps that have more oversized particles and surface defectivity.

Conclusion

Positive displacement pumps (bellows and a diaphragm) cause significant agglomeration (oversized particles) in low-k slurries. The magnitude of pump-induced slurry agglomeration depends on the shear stress and chemical nature of the slurry. The normalized oversized particle distributions show that the maglev centrifugal pump caused less shear flow and did not show any significant particle agglomeration in low-k slurries.

The slow aggregation model demonstrated the stress effect on particle agglomeration and had an excellent agreement with the experimental data. Based on our simulated model and experimental results, the average shear stress in a positive displacement pump is ~100× higher than that of a maglev centrifugal pump. High shear flow generated by positive displacement pumps increased the distribution of oversized particles, leading to significantly increased surface defectivity (scratches or roughness) during CMP, whereas less defectivity was found in slurries circulated by centrifugal pumps. Excellent correlation was established between the roughness/defect density and the degree of agglomeration. **SI**

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